

ION PAIRING AND HYDROGEN BONDING IN THE EXCITED STATE  
OF ALKALI CARBANION SALTS

By

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1974

For those who wanted to come home again. . . .

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Abstract of a Dissertation Presented to the Graduate Council  
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Major Department: Chemistry

The fluorescence and excitation spectra of the alkali metal salts of the anions of fluorene and fluoradene, and the radical anion of anthracene, were studied at room temperature in protic and aprotic solvents. As expected, the excitation spectra were usually identical to the absorption spectra of these salts, and displayed the same behavior with changing cation and solvent.

The shifts in the fluorescence maxima of the salts in aprotic solvents are explained in terms of an equilibrium between contact and solvent-separated ion pairs, the proportion of the latter increasing as the cation is changed from a larger to a smaller, as the solvent is changed from a poorer to a better solvator of cations, or as a cation complexing agent, such as a crown ether, is added.

At smaller salt concentrations in ether solvents of low dielectric constant, free ions were observed. For one such system, fluoradenyl sodium in tetrahydropyran (THP), a dissociation constant was calculated from the excitation spectra which agreed reasonably well with the value obtained from conductance measurements.

Significant effects due to cation-solvent interactions were also observed in the lifetimes and relative intensities of these salts. These are explained in terms of a "normal" heavy atom quenching effect, which should decrease in importance from cesium to sodium, and another effect increasing in importance from cesium to sodium. Several different detailed mechanisms for this second effect are discussed.

Excited fluoradenyl sodium was investigated in protic solvents, and red shifts (higher wavelengths) in the fluorescence maximum seen, compared to the free anion in acetonitrile. This is explained in terms of hydrogen bonding to the free anion. In mixed ether (THP)-alcohol (n-propanol) solvents, a similar red shift was seen. However, upon addition of a cation complexing agent, the maximum shifted back to the position of a normal separated ion pair. This is interpreted in terms of the cation assisting in hydrogen bond formation.

Unsuccessful attempts were made to generate carbanions from excited hydrocarbons. The reasons for these failures are discussed and used to explain the solvent dependence of the acid dissociation constant of fluoradene in terms of aggregation of the hydrocarbon in protic solvents.

Finally, the effects of aggregation on the absorption and fluorescence spectra of carbanion salts were examined, by applying simple exciton theory to bisfluorenyl barium in THP and tetrahydrofuran (THF). Detailed structures are derived for the anion dimer which are reasonable in view of the greater cation solvating ability of THF. Qualitative statements, based on exciton theory, are made about structure of fluorenyl-alkali metal salt aggregates, and certain unusual spectral results explained.

## CHAPTER I INTRODUCTION

Whenever a salt is dissolved in a solvent, dissociation of the salt into its free ions may not go to completion. Depending on such factors as the charge of the ions, their size, the dielectric constant of the solution, the ability of the solvent to solvate any or all the individual ions, and the concentration and ionic strength of the electrolytic solution, the degree of ionization may be nearly unity or almost nil.

However, in order to fully characterize electrolytic solutions, it may be necessary to invoke the presence of other species. The non-dissociated ion pairs may associate with themselves to form neutral aggregates such as dimers, trimers, or, in general, n-mers. At the same time, the non-dissociated ion pair may associate with free ions to form charged aggregates such as triple ions. The chemical behavior of such species should be highly dependent upon their structure, but, except for certain dye molecules at high concentrations,<sup>1-8</sup> the structure of such associated species has not been extensively examined.<sup>9,10</sup> Also, the free ions, or the ion pairs, may interact with the solvent to form charge-transfer species, or, in protic media, hydrogen bonded species, either of which may also affect the chemical behavior of the electrolyte.<sup>11-14</sup>

To further complicate this picture, the non-dissociated ion pair may exist in two forms, contact and solvent separated ion pairs. The latter species, first invoked by Winstein to explain solvolysis

phenomena,<sup>15,16</sup> may be thought of as the result of the diffusion of a single layer of solvent molecules between the anion and the cation of a contact ion pair. This species still travels through the medium as a single entity, as would a contact ion pair, but also may exhibit some of the drastically different behavior expected of free ions. This concept of a solvent-separated ion pair has been of great importance in explaining such diverse phenomena as the mechanism and stereochemistry of organic reactions,<sup>15-17</sup> the rates of initiation and propagation of ionic polymerizations,<sup>18,19</sup> the electronic and vibrational absorption spectra of organic and inorganic salts,<sup>20a</sup> the electron spin resonance spectra of radical ion salts,<sup>20b</sup> and the nuclear magnetic resonance spectra of certain salts.<sup>20c</sup>

In Figure 1 is a pictorial presentation of the different possible forms of the ion pair, and a plot of potential energy vs. inter-ionic distance for a simple 1:1 electrolyte in a medium of dielectric constant 20, originally due to Grunwald.<sup>21</sup> The physical basis of the Grunwald scheme is as follows. Assume two free ions in solution, infinitely separated. As they approach, the potential energy of the system decreases. However, each ion may have a solvation shell which will be compressed as the two ions approach, this compression requiring energy. At some point, the energy necessary to compress the solvation shell further will be greater than the stabilization of the system due to the closer approach of the ions, thus causing an increase in the potential energy. As the two ions continue to approach, the energy of compression of the solvation shells will, at some distance, be the same as the energy of formation of this

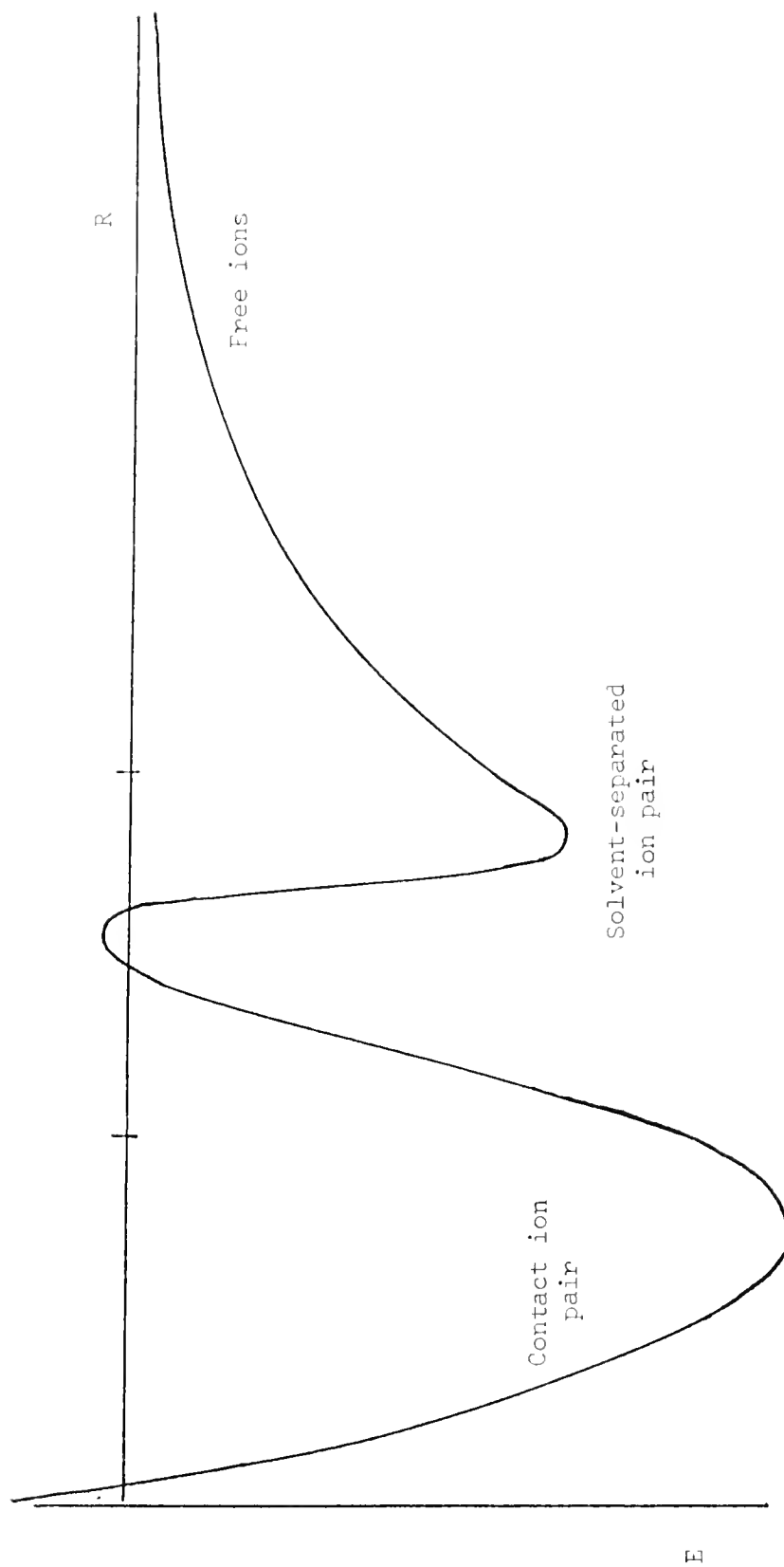


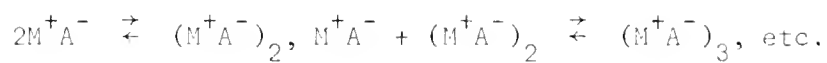
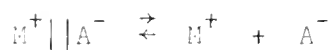
Figure 1. Plot of potential energy,  $E$ , as a function of interionic distance,  $R$ , for a 1:1 electrolyte in a solvent of dielectric constant 20.

shell, and the ions will collapse into the contact pair, i.e. the solvation shell will be squeezed out. Thus, one may visualize at least two other distinct chemical entities, as well as free ions: one, corresponding to the complete collapse of the free ions, the contact ion pair; the other, corresponding to partial collapse of the individual free ions but with the maintenance of a layer of solvent molecules between them, the solvent-separated ion pair.

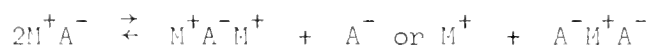
It must be noted that while the difference between contact and separated ion pairs has been presented as between two species, there is evidence for two families of ion pairs,<sup>22</sup> since both the contact and solvent-separated species may exhibit varying amounts of peripheral solvation. A compilation of the various possible equilibria is given in Figure 2.

The foregoing has dealt with well-known ground state phenomena; there is no reason to assume a priori that these same considerations will not hold true in the electronically excited state of an ion pair as well. Indeed, recently there have been several attempts to explain data on excited molecules in terms of dissociation of ionized excited species into free, or hydrogen bonded, ions.<sup>23-37</sup> However, while the presence of ion pairs has been postulated, there has been no systematic investigation to determine the validity of this postulate; and, thus, there has been some skepticism shown.<sup>38</sup> The presence or absence of ion pairing phenomena in such excited state processes as electrochemiluminescence could play a critical role in both the qualitative and quantitative understanding of these processes.

Further, by studying ion pairing in the excited state, one



aggregation to form n-mers



triple ion formation

Figure 2. Equilibria possible in ionic solutions.

could use this information to elucidate the nature of the other, more specific, phenomena of aggregation and hydrogen bonding in the ground state, referred to above. Intimately bound with these aims would be the effort to determine similarities and differences between ground and excited states, the effect of electronic excitation on their ion-pairing properties, and to examine at least some of the pathways available to the excited state to allow it to return to the ground state.

Thus, the goals of the present work, broadly stated, are the following:

(1) The determination of how far the validity of the concept of ion pairing extends for the excited state.

(2) An investigation of the usefulness of information about the excited state of ion pairs for the determination of specific ground state phenomena, such as dissociation, aggregation, and hydrogen bonding.

(3) An examination of the differences between the ground and excited states of ion pairs and the role of cation-solvent relaxation processes, in these differences.

(4) An examination of the "deexcitation reaction," i.e. attempting to show what factors determine how fast, and in what manner, the excited state ion pair returns to the ground state.

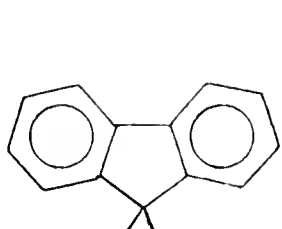
Some of the most extensively investigated systems exhibiting ion pairing in the ground state are the alkali metal salts of fluorene. As shown by Hogen Esch and Smid,<sup>39</sup> in low dielectric constant media, with decreasing temperature or changing from a poorer to a better cation solvating medium, a second peak appears in the absorption

spectra, due to the separated ion pair. Thus, the absorption spectra of these salts are sensitive indicators of cation and solvent effects in the ground state. Consequently, it was thought that their fluorescence spectra would give the same sort of information about the excited state in such media as tetrahydrofuran (THF), tetrahydropyran (THP), 1,2-dimethoxyethane (DME), dioxane, and toluene. Also, macrocyclic polyethers such as dicyclohexyl-18-crown-6 (2,5,8,15,18, 21-hexaoxatricyclo[20.4.0.0]hexacosane), a crown ether, were used to obtain loose ion pairs, especially under conditions where they would not otherwise be formed.<sup>22,40</sup> Thus, these systems should be useful in determining the validity of ion-pairing for the excited state, looking at cation-solvent relaxation processes, and examining the deexcitation process.

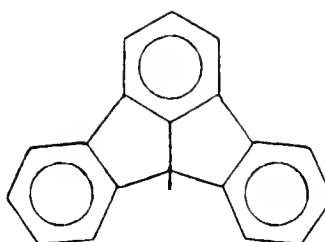
Further, the bisfluorenyl barium salt should be a good model system for a triple ion or ion pair dimer,<sup>41-43</sup> since: (1) conductance studies indicate that one is dealing with essentially only one species (there is no evidence for higher aggregates and the first dissociation constant is low,  $K_d = 3 \times 10^{-9}$  l/mole, in THF), and (2) some data are already available about its structure in solution. This could be applied to the lithium and sodium fluorenyl salts in dioxane, and lithium fluorenyl in toluene, which are all believed to be aggregated on kinetic grounds.<sup>39</sup>

In order to more meaningfully discuss radical ion processes, the sodium and cesium salts of anthracene were investigated in THF, THP, and THP-glyme mixtures. These systems are known to exhibit ion-pairing in the ground state, and are well characterized.<sup>44-48</sup>

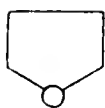
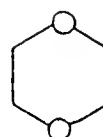
In order to examine hydrogen bonding to excited state carbanion salts, the alkali salts of fluoradene were investigated. Because of the relatively great acidity of the hydrocarbon,<sup>49</sup> this anion can exist in a much greater variety of solvents than the fluorenyl anion, and has been shown to hydrogen bond in the ground state,<sup>50</sup> the cation playing a significant role in the hydrogen bonding of the non-dissociated salt. Thus, the fluoradenyl salts were investigated in THF, THP, DME, dioxane, acetonitrile, methanol, ethanol, n-propanol (n-PrOH), n-propylamine (n-PrNH<sub>2</sub>) and t-butanol (t-BuOH). See Table 2 and Figure 3.



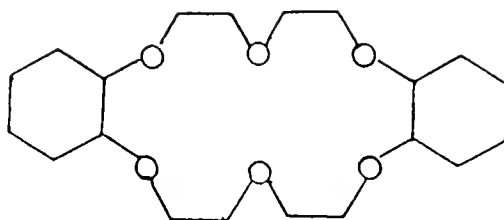
Fluorene



Fluoradene

Tetrahydrofuran  
(THF)Tetrahydropyran  
(THP)

Dioxane



Dicyclohexyl-18-crown-6

Figure 3. Chemicals

Table 1. Summary of ion-pairing in the ground state of alkali fluorenyl salts at room temperature

Cation	Solvent	Type ion pair <sup>a</sup>	Principal absorption maximum
Li <sup>+</sup> <sup>b</sup>	Dioxane	C	346
	Toluene	C	343
	THP	70% C : 30% S	349; 373
	THF	20% C : 80% S	349; 373
	DME	S	373
Na <sup>+</sup> <sup>b</sup>	Dioxane	C	354
	THP	C	356
	THF	95% C : 5% S	356, 372 (shoulder)
	DME	20% C : 80% S	358, 373
K <sup>+</sup> <sup>b</sup>	THP	C	362
	THF	C	362
Rb <sup>+</sup> <sup>b</sup>	THP	C	363
Cs <sup>+</sup> <sup>b</sup>	Dioxane	C	363
	THP	C	364
	THF	C	364
	DME	C	364
Na <sup>+</sup> (CE) <sup>c,d</sup>	THF	S	373
	THF	S	373
	DME	S	373
Ba <sup>+2</sup> <sup>e</sup>	THF	C	348, 371 (shoulder)
	THP	C	346, 371 (shoulder)
Ba <sup>+2</sup> (CE) <sup>c</sup>	THF	50% C : 50% S	349, 373
	THP	50% C : 50% S	349, 373

<sup>a</sup> C = contact, S = separated, F = free.

<sup>b</sup> Data from reference 39, supplemented by author.

<sup>c</sup> CE = slight excess of dicyclohexyl-18-crown-6 present.

<sup>d</sup> Data from reference 40, supplemented by author.

<sup>e</sup> Data from references 41 and 43.

Table 2. Summary of ion pairing in the ground state of alkali fluoradenyl salts at room temperature<sup>a</sup>

Cation	Solvent	Form of the ion pair <sup>b</sup>	Absorption maxima
Li <sup>+</sup>	Dioxane	C	356, 366, 382, 500-520 <sup>c</sup>
	THF	S	369, 388, 529, 570
	DME	S	369, 388, 529, 570
	Acetonitrile	F	370, 389, 530, 570
Na <sup>+</sup>	THP	C	359, 371, 510, 540
	THF	≈50% C : 50% S	361, 371, 388, 530, 570
	n-PrNH <sub>2</sub>	≈80% C : 20% S	362, 381, 525, 555
	3n-PrOH	S-H	362, 380, 525-45 <sup>c</sup>
	t-BuOH	C	357, 369, 505, 535
	n-PrOH	F-H	361, 376, 525-540 <sup>c</sup>
	EtOH	F-H	361, 376, 525-540 <sup>c</sup>
	MeOH	F-H	361, 376, 525-540 <sup>c</sup>
K <sup>+</sup>	THP	C	361, 374, 512, 547
Cs <sup>+</sup>	THP	C	367, 378, 518, 553
n-PrNH <sub>3</sub> <sup>+</sup>	n-PrNH <sub>2</sub>	C	361, 376, 525-40 <sup>c</sup>
Na <sup>+</sup> (CE)	THP	S	369, 388, 529, 570
	THF	S	369, 388, 529, 570
	t-BuOH	S	365, 384, 524, 564
	3n-PrOH	S	367, 386, 525, 567
Ba <sup>++</sup>	THF	C:S	350, 360, 388, 495, 520, 570
	THP	C	340, 350, 495, 523

<sup>a</sup> Data from reference 13, supplemented by author.

<sup>b</sup> C = contact, S = separated, F = free, H = hydrogen bonded.

<sup>c</sup> Broad maximum.

## CHAPTER II EXPERIMENTAL PROCEDURES

### Preparation and Purification of Sample Systems

Tetrahydrofuran (THF), tetrahydropyran (THP), and 1,2-dimethoxyethane (DME) were purified by refluxing over sodium-potassium alloy for about 12 hours, then distilled onto fresh alloy. A small amount of benzophenone was added, and the resultant purple dianion solution degassed on a vacuum line. The benzophenone anion acted as an indicator of the presence of water or oxygen.<sup>39</sup>

Dioxane was refluxed over  $\text{CaH}_2$  for approximately 12 hours, then fractionally distilled and sodium-potassium alloy added. A small amount of fluorenone was added, and the resultant green solution degassed on the vacuum line.<sup>39</sup>

Methanol (MeOH), ethanol (EtOH), and n-propanol (n-PrOH) were refluxed over magnesium filings activated by iodine for approximately three hours, then distilled under vacuum, and degassed.<sup>51</sup>

Toluene, pyridine, n-propylamine (n-PrNH<sub>2</sub>), hexane, and t-butanol (t-BuOH) were stirred over  $\text{CaH}_2$ , for 12 hours, distilled under vacuum onto fresh  $\text{CaH}_2$ , stirred, degassed, then distilled under vacuum and degassed again.

Acetonitrile was stirred over  $\text{CaH}_2$  for 12 hours, distilled under vacuum onto  $\text{P}_2\text{O}_5$ , stirred for 12 hours, and distilled again under vacuum into an ampoule of lithium fluorenyl.<sup>52</sup>

Deionized water was degassed by distilling under vacuum and freezing the distillate, pumping on the resultant solid, then allowing the solid ice to melt. This was repeated three times.

Fluorene was recrystallized from absolute ethanol;<sup>39</sup> fluoradene from hexane.<sup>49</sup> Purity was checked by melting point, and ultraviolet spectrum.

Fluorenyl and fluoradenyl salts were prepared from the corresponding salts of the 1,1,4,4-tetraphenylbutane dianion ( $\text{TPB}^{=}$ ), usually in THF, which were available in the laboratory. Transfer of the salt to other solvents was achieved by evacuating the THF solution to ultimate vacuum (about  $10^{-7}$  torr), distilling the desired solvent onto the salt under vacuum, mixing, reevacuating, then adding more of the solvent desired. As an extra precaution, solvents purified by the various means above were usually added to a dry salt sample. If there was any decoloration of the salt, the solvent was repurified. If not, the solvent was distilled from the solution to the salt sample of interest, under vacuum.<sup>39</sup>

Anthracene was recrystallized from n-propanol, then dried in vacuo. Sodium radical anion salts of the hydrocarbon were formed by reacting a solution of the hydrocarbon with a sodium mirror under vacuum. The cesium salt was formed by reacting the hydrocarbon in THF with the metal, under vacuum.

All solutions were stored under vacuum in ampoules equipped with break-seals. When not in use, all samples were kept in a freezer at  $-20^{\circ}\text{C}$ , where they usually were stable.

The crown ether used was dicyclohexyl-18-crown-6, obtained from Dr. H.K. Frensdorff of E.I. du Pont de Nemours Elastomers Department, and recrystallized from petroleum ether.<sup>53</sup> Later samples were recrystallized from acetonitrile and stored under vacuum. Samples of crown ether were added to salt solutions by means of

evacuated break-seals; if any decoloration or significant loss in optical density occurred, the samples were not used. Due to their low solubility, especially in THP, the crown ether-salt samples were usually filtered before use. (See Figure 3.)

Reagent grade sodium tetraphenylborate was purified according to a modification of the method of Skinner and Fuoss,<sup>54</sup> as follows. The salt was partially dissolved in an eight-to-one mixture of methylene dichloride and acetone. The solution was filtered, and toluene added until a white precipitate started to appear. The mixture was then immersed in a dry ice-isopropanol bath, and the white precipitate collected on filter paper. The solid was placed in an ampoule and dried on the vacuum line for approximately two hours. This procedure was necessitated by the destruction of fluorenyl samples by the reagent grade salt, which smelled like phenol. After purification in the above manner, the sodium tetraphenylborate did not destroy anion solutions, even when added in excess by a hundred-fold, to determine common ion effects.

#### Spectral Measurements

Salt samples were usually formed in an apparatus similar to that of Figure 4, at a concentration of about  $10^{-2}$  M, in the following manner. After the apparatus was built (all glass except for the quartz optical cells and the spacer), it was attached to the vacuum line and tested for pin-holes with a Tesla coil (and repaired, if necessary). It was then flamed out, evacuated to about  $10^{-7}$  Torr, and sealed from the line at constriction a. The hammer and an

external magnet were used to break the break-seals of the fluorene and TPB<sup>+</sup> solutions' ampoules and the two were mixed. The absorption spectrum of the resulting solution was taken with a Beckman Acta V, in the range 325-600 nm, in the 2 mm cell with either a 1.8 mm or 1.9 mm spacer, to determine the concentration.<sup>39</sup> A typical absorption spectrum (of sodium fluorenyl in THP) is reproduced in Figure 5.

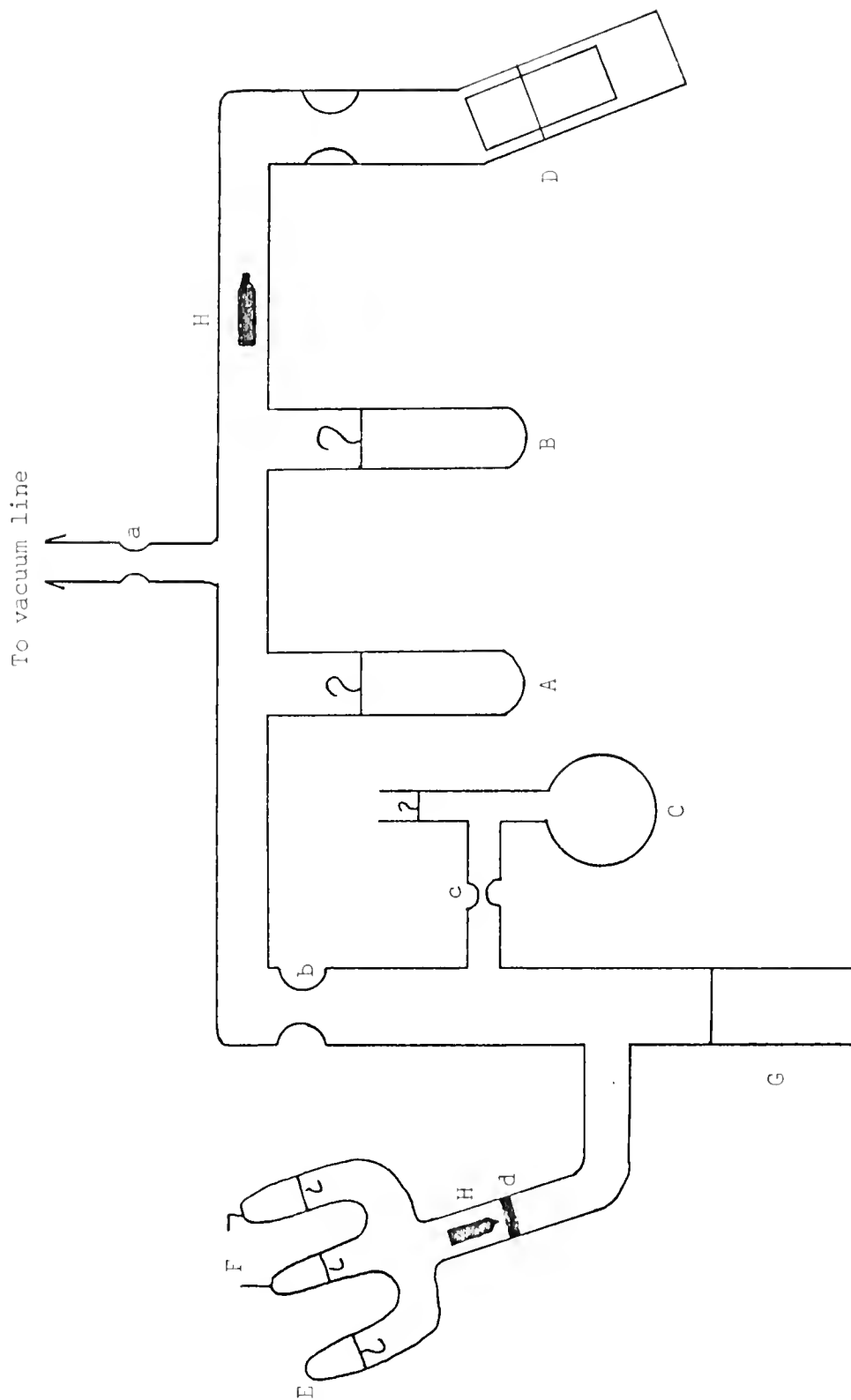
The solution was then poured through the constriction b, and the walls of the apparatus "washed" with solvent, by application of a dauber, dipped in liquid nitrogen, to the outside. After the walls were clean, the receiver was sealed away from the rest of the apparatus at b.

Dilutions of the sample were accomplished by pouring most of the solution into the sidebulb, through constriction c, and distilling solvent back into the cell by application of a cold dauber. Concentrations less than  $10^{-3}$  M could be calculated from the visible and near ultraviolet spectrum, and known extinction coefficients.<sup>39</sup>

Fluorescence emission and excitation spectra were taken on a Perkin-Elmer MPF-2A spectrofluorimeter in the ratio record mode, courtesy of Dr. Stephen G. Schulman of the College of Pharmacy, in the following manner. One of the principal absorption maxima was chosen as the exciting wavelength, and the emission spectrum manually scanned to find the maximum. Then, holding the wavelength of emission fixed, the excitation spectrum was scanned manually to find an optimum excitation wavelength. At this point, exciting with light of the optimum wavelength, the emission spectrum was

Figure 4. Apparatus used in preparing fluorenyl sodium in THF.

- A. Ampoule of fluorene;
- B. Ampoule of  $\text{Na}_2\text{TPE}^+$  in THF;
- C. Sidebulb;
- D. 2 mm optical cell with spacer;
- E. Ampoule of sodium tetraphenylborate;
- F. Ampoules of crown ether;
- G. 1 cm fluorescence cell;
- a,b,c. Constrictions;
- d. Course sintered glass filter.



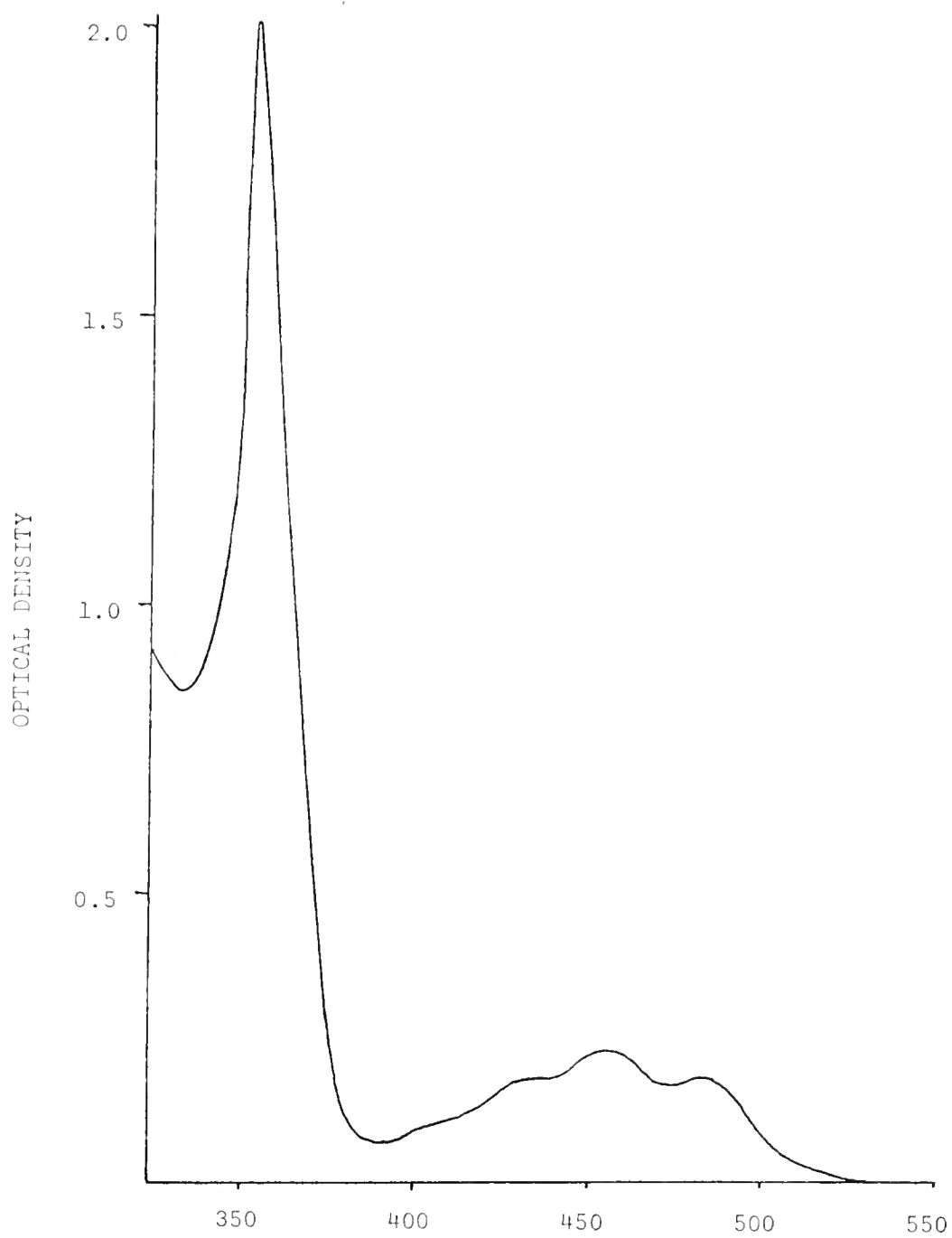


Figure 5. Absorption spectrum of fluorenyl sodium in THF.

scanned and recorded. Then, selecting an emission wavelength of significant intensity, the excitation spectrum was scanned and recorded.

Lifetimes were measured by Mr. Anthony Capomacchia of Dr. Schulman's group at the College of Pharmacy, on a TRW nanosecond decay time fluorometer, using a pulsed nitrogen lamp and a Tektronix 556 dual-beam oscilloscope with two IAI plug-in dual-channel amplifiers.

The values given here represent the lifetimes obtained from at least two different concentrations of the same salt (except for cesium fluorenyl, which was anomalous). The accuracy of the lifetimes of the fluorenyl salts is probably much less than that of the fluoradenyl salts for the following reasons. In the systems studied, there was always residual hydrocarbon present, either fluorene or fluoradene. However, there was never any evidence of the formation of an excimer of fluorene, meaning that the output signal of the irradiated solution always contained a component attributable to the hydrocarbon. For the salts of fluorene with lower lifetimes, this was a major source of error. Thus, the data are considered to be no better than 10% and probably no worse than 25%, with the longer lifetime salts being most accurate. For the fluoradene salts, however, the accuracy was probably nearer 10%, since, in the solvents examined, there was very little hydrocarbon monomer emission; the fluoradene hydrocarbon mainly emitting through an excimer state of much lower intensity, relative to the fluoradenyl salt emission, then the intensity of the fluorene monomer relative to its salts.

This difference could be easily distinguished by visual comparison of the oscilloscope signals of the fluorenyl and fluoradenyl salt systems. Little use is made of the absolute numbers, in any event, and the general trends noted are of greater importance.

Relative intensities were obtained either by comparison of peak height to an internal standard (the free ion for the fluoradenyl salts; the crown ether-separated, or solvent-separated ion pair for the fluorenyl salts), or by comparison of peak heights between two different salt solutions at known concentrations. This is a less accurate procedure than the former, since different samples might have different concentrations of quenching impurities. However, results obtained in this manner were reproducible to within 20%.

Implicit in the above work for the fluorenyl ion pairs was the assumption that there was no difference between a solvent-separated ion pair and a crown-ether-separated ion pair. To check this, a solution of fluorenyl sodium in DME (20% contact, 80% solvent-separated ion pairs in the ground state) was prepared, and its fluorescence spectrum compared to that of the same solution to which a slight excess of crown ether had been added. There was no difference in terms of peak positions (528, 568 nm for both) or peak heights, which justified the assumption.

After a series of spectra had been obtained for a particular salt, using the salt in the receiver part of the apparatus in Figure 4, weighed amounts of reagents such as crown ether or common ion could be added by using the hammer and an external magnet to open the appropriate break-seal, mix the salt solution with the

pre-weighed solid contained in vacuum, filter the solution through d, and repeat the series of spectra. After the completion of an experiment, the apparatus could be turned on its side so that the side-bulb was down, and the solution poured into the side-bulb, the tubing "washed" around constriction c, and the solution sealed away from the rest of the receiver apparatus and stored in the freezer.

### CHAPTER III CATION AND SOLVENT EFFECTS

#### Fluorenyl Systems: Experimental Results and Discussion

##### General Considerations

The first systems investigated were the alkali metal salts of fluorene. Typical emission spectra are shown in Figure 6, those of fluorenyl sodium (NaFl) in THP, at different concentrations. All the emission spectra of the fluorenyl systems displayed two peaks as shown, so that it is highly unlikely that they represent two different species. Further, their relative intensities, at a given concentration, were unaffected by the addition of common ion or mode of preparation, and they persisted, with about the same relative intensities, from  $10^{-4}$  M down to the lowest concentration studied ( $10^{-9}$  M). For these reasons, it was concluded that the doublet arose from emission from the lowest vibrational state of the first excited state ( $S_1$ ) into two vibrational states of the electronic ground state. Additional evidence for this lies in the fact that, according to Berlman,<sup>55</sup> the parent hydrocarbon, fluorene, also has two peaks in its fluorescence spectrum. Also, the separation of the two peaks (at least below  $10^{-3}$  M) is constant at  $1240 \pm 10 \text{ cm}^{-1}$ , near where the hydrocarbon,<sup>56</sup> and fluorenyl-calcium chloride<sup>57</sup> have both been reported to have a vibration of appropriate symmetry to couple with the electronic transition ( $1277$  and  $1219 \text{ cm}^{-1}$ , respectively).

At higher concentrations ( $10^{-2}$  M to  $10^{-4}$  M), both the position and relative intensity of the two peaks are dependent upon concentration.

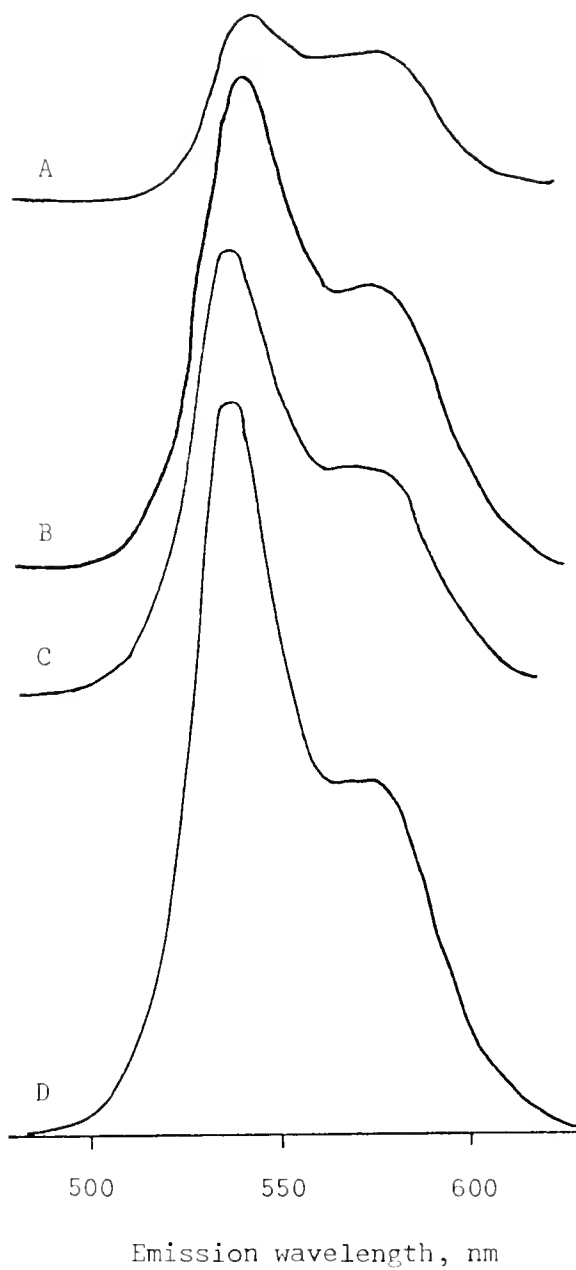


Figure 6. Effect of concentration on the emission spectrum of fluorenyl sodium in THP. A.  $[\text{NaFl}] = 2 \times 10^{-2} \text{ M}$ ; B.  $[\text{NaFl}] = 6.5 \times 10^{-3} \text{ M}$ ; C.  $[\text{NaFl}] = 2 \times 10^{-4} \text{ M}$ ; D.  $[\text{NaFl}] = 4 \times 10^{-5} \text{ M}$ .

As the concentration decreases toward  $10^{-4}$  M, both peaks shift to lower wavelengths, and the lower wavelength peak gains in relative intensity. At concentrations below  $10^{-4}$  M, while some shifts in the position of peaks are still observed at lower concentrations, the relative intensities of the peaks are now independent of concentration. This is shown graphically for the fluorenyl salts in Figure 7, where the ratio of the lower to the higher wavelength peak heights is plotted as a function of concentration, for several of the salts.

If one examines the excitation spectra of these salts (see Figure 8), as a function of concentration, one finds that in the high concentration region, above  $10^{-4}$  M, anomalous spectra are obtained. However, at concentrations below  $10^{-4}$  M, the spectra are nearly identical to the absorption spectra, as expected<sup>58,59</sup> (although there are significant differences in relative intensities, which will be discussed later).

There are, basically, two important causes of the above phenomena. First, reabsorption processes must be expected to play a significant role. For example, for sodium fluorenyl in THF, while the first absorption maximum occurs at 486 nm, there is significant absorption even at 530 nm ( $\epsilon_{530} \approx 150$ ). Under the conditions of the emission experiments, there should be a great deal of reabsorption of emitted light at the lower wavelengths. Assuming the average path of an emitted photon to be 0.5 cm, for sodium fluorenyl in THF, 95% transmittance of the fluorescent beam would not be achieved until concentrations below  $3 \times 10^{-4}$  M. Thus, as concentration is decreased there should be an increase of intensity at lower wavelengths as

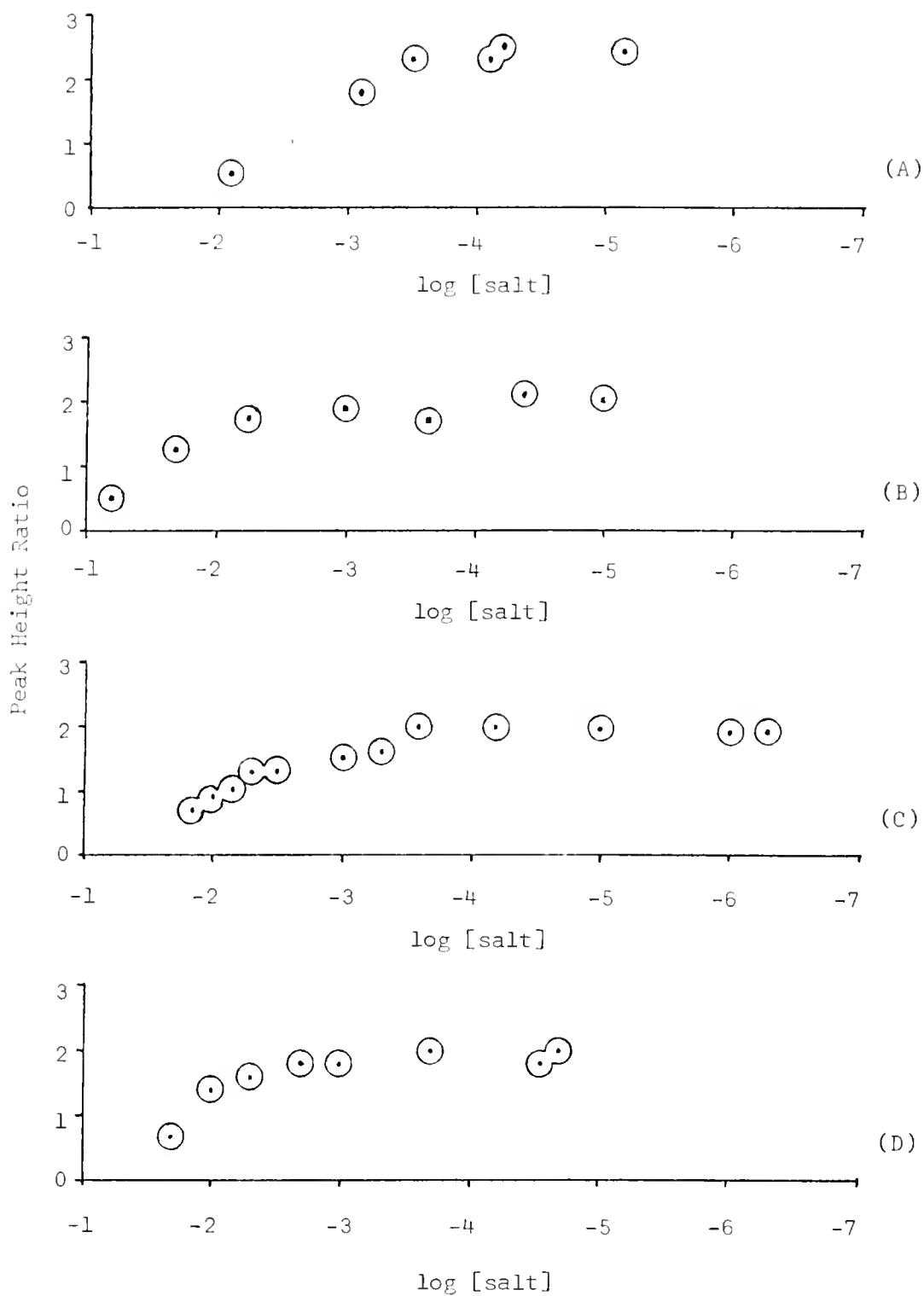


Figure 7. Peak height ratio as a function of concentration for several fluorenyl salts in THP. A. Fluorenyl sodium with an excess of crown ether; B. Fluorenyl sodium; C. Fluorenyl potassium; D. Fluorenyl cesium.

Figure 8. Effect of concentration on the excitation spectrum of fluorenyl sodium in THP.

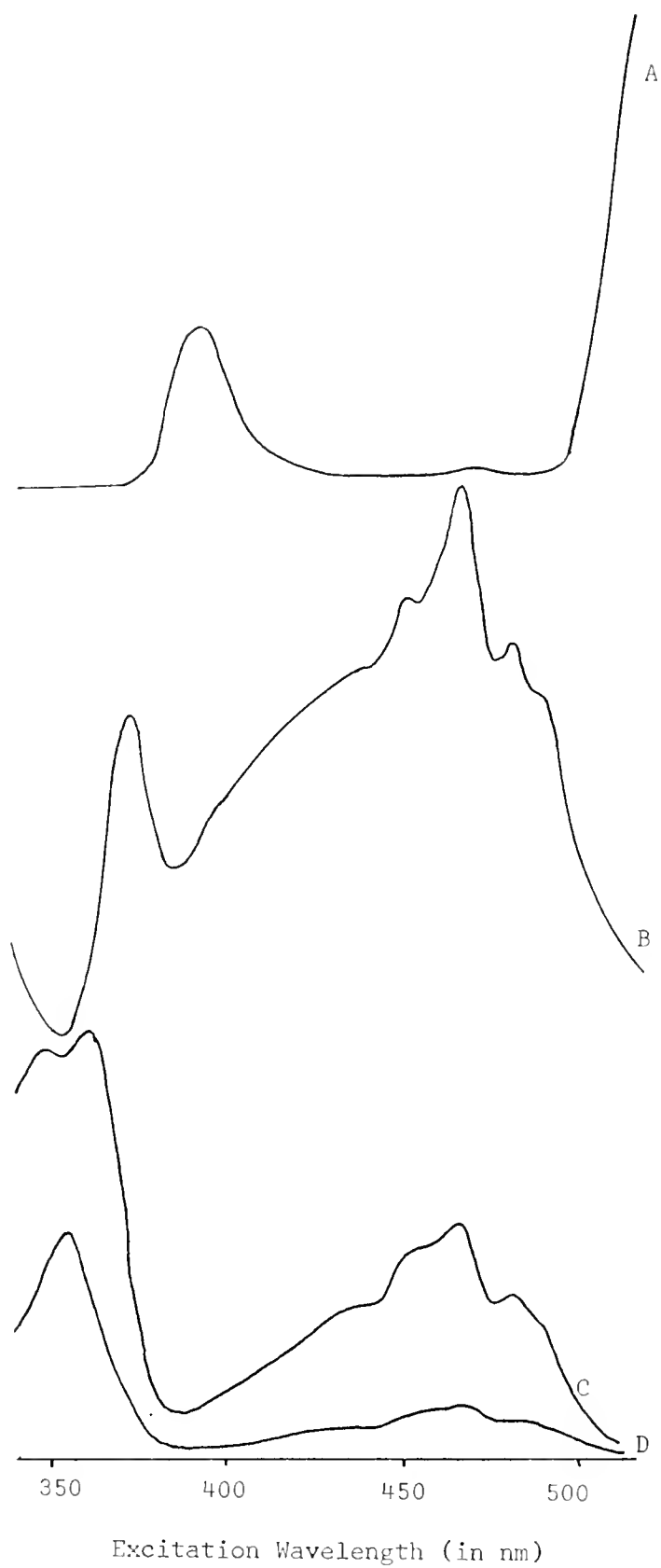
A.  $[\text{NaFl}] = 2 \times 10^{-2} \text{ M}$ ;

B.  $[\text{NaFl}] = 1 \times 10^{-3} \text{ M}$ ;

C.  $[\text{NaFl}] = 2 \times 10^{-4} \text{ M}$ ;

D.  $[\text{NaFl}] = 4 \times 10^{-5} \text{ M}$

(identical spectra for still lower concentrations).



more of the lower wavelength fluorescence passes through the solution without reabsorption, which is observed.

The effect of concentration on excitation spectra is less well defined, but, as shown by McDonald and Selinger,<sup>60</sup> for high absorbance solutions there should be peaks in the excitation spectrum corresponding to troughs in the absorption spectrum, and the results should be dependent upon the geometry of the sampling system. Thus, for high absorbance solutions, if the incident beam must pass through the solution, it will be attenuated so that most of it will be absorbed near the front of the fluorescence cell; i.e. the solution will act as a filter, and most of the emission produced will be near the front of the cell, and out of view of the detection photomultiplier of a conventional spectrofluorimeter employing right angle geometry.

In appendix 1, it is shown that, given the right-angle geometry of the spectrofluorimeter, the change in the excitation spectrum with concentration is that expected for the salt, assuming this "inner filter" effect.

Another factor in the behavior of the salts at high concentration is the formation of triple ions, and higher aggregates. Since this will introduce a much greater degree of complexity, discussion of the effect of aggregation will be postponed until the behavior of bisfluorenyl barium is examined.

Another complication is the possibility of excited complex formation.<sup>61-64</sup> By addition of a ten-fold excess of fluorene, it was shown that if an excited complex was formed, fluorene was not involved, since there was no change in the fluorescent behavior of a solution of sodium fluorenyl, in THF.

### The Effect of Cation

In order to determine the effect of cation on the fluorenyl emission, the fluorescence spectra of the alkali metal salts in THP were taken at concentrations below  $10^{-4}$  M. According to Table 1, the sodium, potassium, rubidium and cesium salts are entirely contact ion pairs in the ground state. The emission results are contained in Table 3.

Hogen Esch and Smid explained the shifts seen in the absorption spectra of these salts in the following manner. The anion, in the ground state of a contact pair, is stabilized by the cation, which occupies its equilibrium position with respect to the ground state charge distribution. Upon absorption of light, the new electronic configuration of the anion is rapidly attained ( $\approx 10^{-14}$  sec), but, in accordance with the Born-Oppenheimer approximation, the cation does not have time to move to its new equilibrium position with respect to the excited anion, which, therefore, is not as stabilized by the cation as is the ground state. Thus, the energy difference between the ground and excited states is increased relative to the free ion, and this increase should be greater the greater the cationic field, i.e. the smaller the radius, for alkali cations; thus, the absorption spectra should be blue-shifted (shifted to lower wavelengths) for contact pairs going from cesium to lithium (See Figure 9).

The above assumes that there is a sufficient difference in the charge distribution of the ground and excited states to cause cation-anion reorientation. As pointed out by Birks and Dyson,<sup>65</sup> the lack of mirror symmetry between the absorption and fluorescence spectrum

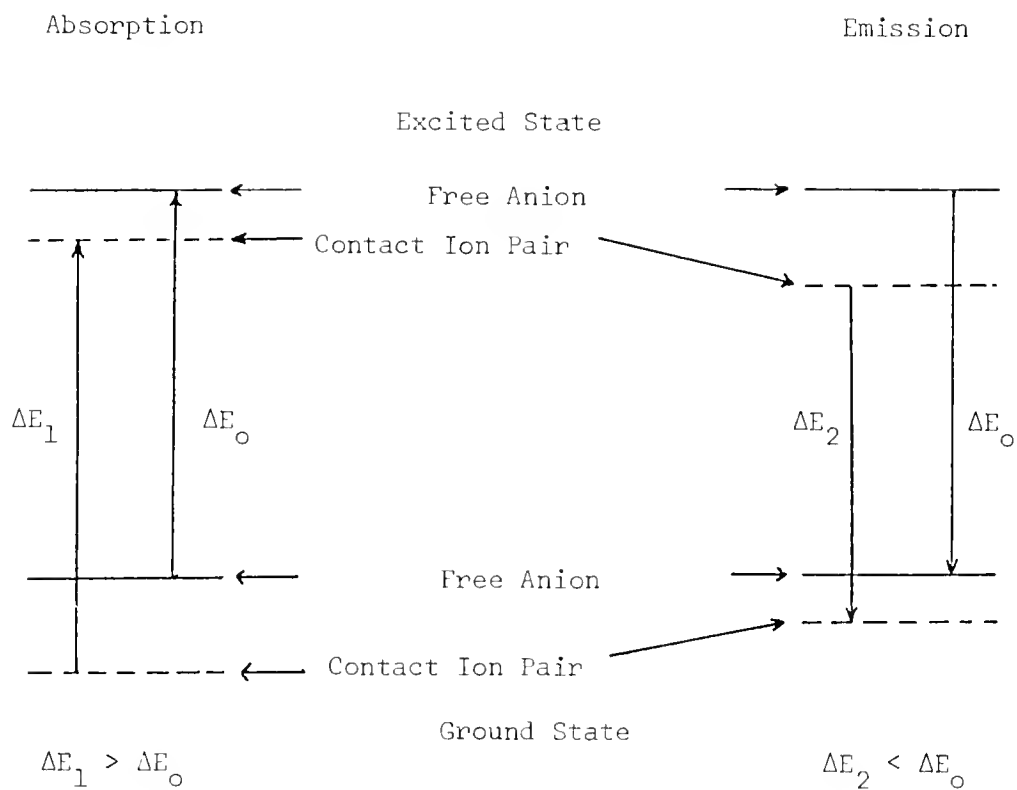


Figure 9. The effect of cation on the spectra of contact ion pairs.

Table 3. Effect of cation on ion pairing of fluorenyl salts in THF.

M <sup>+</sup>	Fluorescence maximum (nm)	Ground State <sup>b</sup>	Excited State <sup>a</sup>
Li <sup>+</sup> <sup>c</sup>	528	70% C : 30% S	S
Na <sup>+</sup>	538	C	C
Na <sup>+</sup> (CE) <sup>d</sup>	528	S	S
K <sup>+</sup>	535	C	C
K <sup>+</sup> (CE) <sup>d</sup>	528	S	S
Rb <sup>+</sup>	534	C	C
Cs <sup>+</sup>	533	C	C

<sup>a</sup> C = contact, S = separated.

<sup>b</sup> See Table 1, for references.

<sup>c</sup> Excitation at either 349 or 373 produced emission at 528.

<sup>d</sup> Slight excess crown ether added.

of a compound is a sensitive indicator of changes in the electronic distribution in that compound between the ground and excited states. A comparison of Figures 5 and 6 would indicate such a lack. Further, as shown in Appendix 2, simple Hückel calculations for the fluorenyl anion also indicate major changes in the electronic distribution of the anion in going from the ground to the first excited state.

Analogous reasoning should explain the shifts in the fluorescence spectra, if one assumes that the lifetime of the excited state is long enough to permit the cation to reach its equilibrium position with respect to the excited anion (see Figure 9). During emission, the cation does not have time to reach its ground state equilibrium position, and the excited anion may be more stabilized than it is in its ground state just after emission. This means that the energy difference is now decreased relative to the free ions, this difference being greater the greater the cationic field, i.e. the smaller the cationic radius. Thus, a red shift (shift to higher wavelengths) would be expected for a series of contact ion pairs as the cationic radius is decreased, i.e. going from cesium to sodium fluorenyl in THP, with lithium open to question in THP, due to the significant amount of solvent-separated ion pairs present in the ground state (see Table 1).

From Table 3, it is obvious that the expected shifts do occur from cesium to sodium, but that lithium fluorenyl emits at 528 nm. The position of this peak was unaffected by the addition of lithium tetrphenylborate, a source of lithium ions, so that the possibility of dissociation of the contact pair into free ions in the excited state seems unlikely. To further identify the emitting species in

this case, the fluorescence spectrum of lithium fluorenyl in THP was compared to those of both the sodium and potassium salts to which had been added a slight excess of dicyclohexyl-18-crown-6. Since all three have the same emission maximum, 528 nm, it seems safe to identify the emitting species in the lithium fluorenyl case as the solvent-separated ion pair.

This significant finding justifies the assumption that the lifetime of the excited state is long enough to permit the cation to attain its equilibrium position with respect to the new charge distribution of the excited anion, before it emits. Not only is there enough time for the cation to move to its new position, but there is enough time for a layer of solvent molecules to diffuse between cation and excited anion. As will be seen later, the measured lifetimes of the excited state ( $10^{-7}$ - $10^{-8}$  sec) are orders of magnitude<sup>66</sup> longer than solvent relaxation times ( $10^{-10}$ - $10^{-11}$  sec).<sup>67</sup>

From Hückel calculations (Appendix 2), it is to be expected that the excited fluorenyl ion pair should be somewhat looser than the ground state one. Assuming the cation to lie above the cyclopentadienyl ring in solution,<sup>39</sup> the ground state anion has almost two-thirds of the negative charge on those five atoms, while the excited anion has less than one-third there.

Although the constant for the equilibrium between the excited contact and the excited separated ion pair cannot be measured in this case, its value can be estimated from the spectroscopic data, by use of the so-called Förster cycle,<sup>61,66</sup> with the known value of the equilibrium constant in the ground state.

In Figure 10, this cycle is shown as it specifically pertains

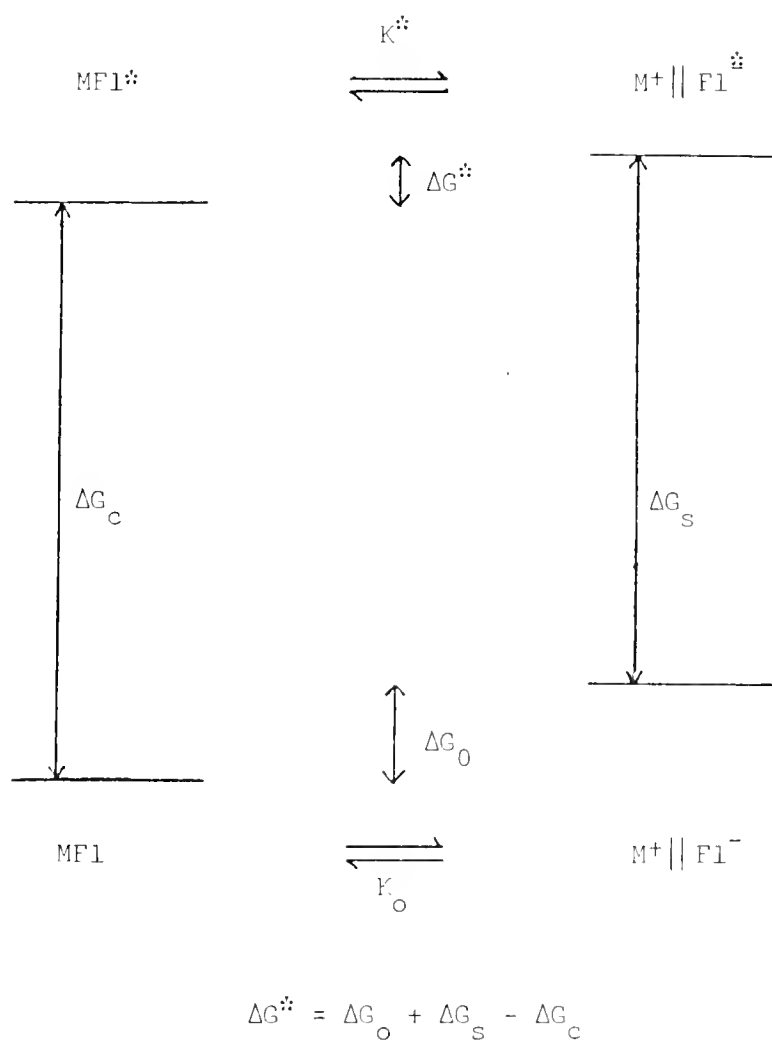


Figure 10. Förster cycle and ion pairing in the excited state.

to the equilibrium between contact and separated ion pairs in the excited state. Denoting the difference in free energy between the ground and excited state of a contact and separated ion pair by  $\Delta G_C$  and  $\Delta G_S$ , respectively, the free energy difference for the excited state process,  $\Delta G^\ddagger$ , is related to the free energy difference for the ground state process,  $\Delta G_O$ , by:

$$\Delta G^\ddagger = \Delta G_O + \Delta G_S - \Delta G_C .$$

If the entropy difference for the process is about the same in both the ground and excited states, then  $\Delta G_S - \Delta G_C$  can be approximated by the enthalpy differences:  $\Delta G_S - \Delta G_C \approx \Delta H_S - \Delta H_C$ . Since the enthalpy difference between the ground and excited states of the contact or separated pair in solution is virtually identical to the internal energy,  $\Delta E$ , which can be approximated by averaging the 0-0 lines of the absorption and emission spectra, it can be shown that:<sup>41</sup>

$$pK^\ddagger = pK_O - \frac{hc(\bar{\nu}_C - \bar{\nu}_S)}{2.303 kT}$$

where  $pK$  is the negative common logarithm of the equilibrium constant,  $h$  is Planck's constant,  $c$  is the speed of light,  $k$  is the Boltzmann constant,  $T$  the temperature (in K), and  $\bar{\nu}_C$ ,  $\bar{\nu}_S$  the average of the 0-0 lines of the absorption and emission spectra for the contact and separated ion pairs, respectively. If the value of the ground state equilibrium constant is 3/7, then  $pK^\ddagger = \log (7/3) - 2.35 = -2.08$ , or,  $K^\ddagger = 120$ , which is in striking accord with the fluorescence spectrum.

#### The Effect of Solvent

A compilation of the behavior of the alkali metal salts of

fluorene in different solvents is given in Table 4, as well as assignments of the type of ion-pairing in the ground and excited states.

Hogen Esch and Smid<sup>39</sup> explained the effect of solvent on the absorption spectra of these salts in the following manner. For a contact ion pair, as the solvent is changed to one better able to solvate cations, it decreases the amount of perturbation of the anion by the cation, and the absorption spectra will shift toward that of the free ion. Thus, the lithium fluorenyl contact ion pair absorbs at 343 nm in toluene, 346 nm in dioxane, and 349 nm in THF.

This greater cation solvating ability of one solvent over another may also manifest itself as an increase in the amount of separated ion pairs present. Thus, sodium fluorenyl absorbs at 355 nm in THP, absorbs at 356 nm with a shoulder at 372 nm in THF, and at 373 nm with a small peak at 358 nm in DME, reflecting an increasing amount of separated ion pairs, and hence, a greater cation solvating ability of these solvents.

This same rationale, as can be seen in Table 4, seems to hold true equally well for the excited state. Indeed, the same order of cation coordinating power can be obtained from the table as was found by Hogen Esch and Smid:<sup>39</sup>

DME > THF > THP > Dioxane > Toluene.

However, this is not the only explanation possible, and other explanations will be examined in the General Discussion.

As noted in Table 4, the position of the sodium salt in THF seems somewhat anomalously shifted, relative to the same salt in THP. Since both contact and solvent-separated ion pairs are present

Table 4. Effect of solvent on the fluorescence of alkali metal salts of fluorene, at concentrations below  $10^{-4}$  M.

Cation	Solvent	Emission Maximum(nm)	Type of ion pair <sup>a</sup>	
			Ground <sup>b</sup>	Excited
Li <sup>+</sup>	Dioxane	545 <sup>c</sup>	C	C
	Toluene	552 <sup>c</sup>	C	C
	THP	528	70% C : 30% S	S
	THF	528	20% C : 80% S	S
	DME	528	S	S
Na <sup>+</sup>	Dioxane	540 <sup>c</sup>	C	C
	THP	538	C	C
	THF	532	95% C : 5% S	25% C : 75% S <sup>d</sup>
	DME	528	20% C : 80% S	S
K <sup>+</sup>	THP	535	C	C
	THF	535	C	C
Rb <sup>+</sup>	THP	534	C	C
Cs <sup>+</sup>	Dioxane	534	C	C
	THP	533	C	C
	THF	533	C	C
	DME	532	C	C
Na <sup>+</sup> (CE)	THF	528	S	S
	THP	528	S	S
	DME	528	S	S
Free <sup>e</sup>	THF	528	F	F

<sup>a</sup> C = contact, S = separated, F = free.

<sup>b</sup> See Table 1.

<sup>c</sup> System is aggregated, see text.

<sup>d</sup> From Förster cycle calculations, see text.

<sup>e</sup> Seen in solutions of sodium fluorenyl in THF, at concentrations below  $\approx 10^{-6}$  M.

in the ground state, the possibility of an excited state equilibrium is indicated. Addition of sodium tetraphenylborate, a source of common ion, had no effect on the emission maximum, which indicates free ions are not involved. Further, a combination of a contact ion pair spectrum (such as sodium fluorenyl in THF) with a separated ion pair spectrum (such as the crown etherate of sodium fluorenyl) in a ratio of 1:2 yields a spectrum nearly identical to that of sodium fluorenyl in THF.

Since the ground state equilibrium constant is known (0.064), a Förster cycle calculation could be performed, giving  $pK^* = -0.538$  or  $K^* = 3.4$ . Thus, it seems likely that the fluorescence spectrum of sodium fluorenyl in THF is composed of the emission from both types of ion pairs.

#### Lifetimes and Relative Intensities

Lifetimes and relative intensities for several of the alkali fluorenyl systems at the same concentrations ( $1.10^{-5}$  M) are listed in Table 5. For all the salts examined, except that of cesium, the lifetime at concentrations above  $1.10^{-4}$  M was considerably lower than the listed value. For example, the lifetime of sodium fluorenyl in THF at  $2.10^{-4}$  M is 30 ns, and at  $6.10^{-4}$  M is 24 ns. However, at concentrations below  $10^{-5}$  M, further dilution left the lifetime of the salt unchanged.

The cesium salt, on the other hand, showed a continued decrease of lifetime with concentration throughout the concentration range studied. However, in light of the excess of fluorene present in all systems, it is possible that it interfered with the cesium results, since the lifetime of fluorene is comparable.<sup>55</sup>

The general behavior of the salts, in terms of relative intensities at the emission maximum, is the same. As Table 5 indicates, the free ion has the longest lifetime and emits most intensely; the solvent-separated, or crown ether-separated, ion pair emits nearly as intensely and has nearly the same lifetime; the sodium, potassium, and rubidium salts all have nearly the same intensity and lifetime; while the cesium salt, and the lithium salt in dioxane are of low intensity emitters, with the shortest lifetimes.

The general behavior can be explained as a combination of three effects. The low lifetime and intensity of the lithium salt in dioxane, a system which is probably aggregated (on the basis of kinetic data<sup>39</sup>), will be considered in greater detail later.

The anomalously low emission intensity and lifetime of the cesium salt is probably due to the so-called heavy atom effect, whereby atoms of high atomic number cause a breakdown of the spin-selection rules, and thus enhance intersystem crossing from the first excited state to the lowest triplet state of the chromophore. However, if this were the only effect operative, one would expect to see a significant increase in lifetime and intensity as the cationic atomic number decreased from 55 (cesium) to 37 (rubidium) to 19 (potassium) to 11 (sodium). The invariance of lifetime and relative emission intensity to changes in atomic number for the last three leads to one of two conclusions: (1) there is no heavy atom effect operative for these nuclei, or (2) there is some other effect operating in the opposite direction to the heavy atom effect, thus tending to counterbalance it.

The first possibility, that there is no heavy atom effect for

Table 5. Lifetimes and relative intensities of alkali metal salts of fluorenyl at room temperature, at  $1.10^{-5}$  M.

Cation	Solvent	Emission maximum (nm)	Lifetime (ns)	Relative intensity
$\text{Li}^+$	Dioxane	545	24.	10
$\text{Na}^+$	THP	538	40.	43
$\text{K}^+$	THP	535	41.	41
$\text{Pb}^+$	THP	534	40.	43
$\text{Cs}^+$	THP	533	15.	18
$\text{Cs}^+$	THF	533	15.	18
$\text{Na}^+(\text{CE})$	THP	528	82.	85
Free ion <sup>a</sup>	THF	528	96.	92 <sup>b</sup>

<sup>a</sup> Obtained in dilute ( $C < 10^{-7}$  M) sodium fluorenyl solution.

<sup>b</sup> Obtained by extrapolating back to  $1.10^{-5}$  M.

these nuclei, seems highly unlikely, since the rubidium cation is isoelectronic to the bromide anion, which has been shown to quench the fluorescence of several compounds more effectively than the chloride ion, which is isoelectronic to the sodium cation.<sup>68-70</sup>

(Indeed, a careful reading of reference 70 would indicate a general cation quenching effect.) Thus, it seems likely that the heavy atom effect is operative for these nuclei, but is opposed by another quenching mechanism. While there is no unequivocal evidence in the present work for any specific mechanism, several possibilities will be examined in the general discussion.

## Fluoradenyl Systems: Experimental Results and Discussion

### General Considerations

As with the alkali fluorenyl salts, the alkali metal salts of fluoradene were affected, at higher concentrations, by inner filter and reabsorption effects. However, the problem was somewhat more serious for the fluoradenyl systems, since the molar extinction coefficients were considerably higher.

This was especially serious for the separated ion pairs. The Stokes shifts (difference between highest wavelength absorption and lowest wavelength emission) for both the fluorenyl and fluoradenyl separated ion were comparable (8 nm for lithium fluorenyl in DME vs. 10 nm for lithium fluoradenyl in DME), but the molar extinction coefficient for the fluoradenyl system was almost ten times higher (for lithium fluoradenyl in DME,  $\epsilon(570) = 7800$ , compared with lithium fluorenyl in DME,  $\epsilon(520) = 800$ ). Thus, the emission spectrum of the separated pair was both red-shifted, and the intensity considerably decreased, just as for the fluorenyl system, and these effects persisted down to concentrations about ten times lower than they had in the separated fluorenyl ion pairs, i.e. about  $10^{-5}$  M.

The problem was also more serious for the contact ion pairs of fluoradene than for the contact ion pairs of fluorene. However, the inner filter and reabsorption effects were less severe than for the separated fluoradenyl ion pairs, due to two factors. First, the Stokes shifts of the contact ion pairs of fluoradene are much larger than those of the separated pair (in fact, they are somewhat larger than for the fluorenyl ion pairs). This means that there

is less interference by the visible absorption band on the emission band. Second, the extinction coefficient of the visible band is somewhat less for the contact ion pairs than for the separated ion pairs of fluoradene; e.g. for sodium fluoradenyl in THP,  $\epsilon(540 \text{ nm}) = 5300$ , for the crown ether complex,  $\epsilon(570 \text{ nm}) = 7800$ . Thus, for the contact ion pairs, these inner filter and reabsorption effects persisted down to about  $10^{-4} \text{ M}$ .

#### Effect of Cation

As noted by Hogen Esch,<sup>13</sup> the fluoradenyl anion is sensitive to the same parameters of cation, solvent, and temperature that the fluorenyl anion is. However, in the ground state, fluoradenyl ion pairs tend to be somewhat looser than their fluorenyl counterparts. For example, a lithium fluoradenyl solution in THF contains virtually all solvent-separated ion pairs, while a lithium fluorenyl solution in THF has 25% contact ion pairs. Further, the greater acidity of the parent hydrocarbon, fluoradene, allows one to study the anion in a greater range of solvents.<sup>49</sup>

As can be seen from the data in Table 6, the fluoradenyl salts in THP display much the same behavior as the fluorenyl salts, with two exceptions. First, for all the fluoradenyl salts, the dissociation of the ion pairs into free ions could be detected directly at low concentrations in THP.

Secondly, the sodium salt shows this behavior even at relatively high concentrations ( $10^{-4} \text{ M}$ ), so that one finds a dependence of the position of the emission maximum upon the excitation wavelength. If excited at wavelengths corresponding to the contact ion pairs'

Table 6. Effect of cation on the ion pairing of excited alkali fluoradenyl salts, at room temperature in THP.

Cation	Fluorescence maximum (nm)	Type Ion Pair <sup>a</sup>	
		Ground <sup>b</sup>	Excited
Na <sup>+</sup>	585-600, <sup>c</sup> 600 <sup>d</sup>	C/F	C
Na <sup>+</sup> <sup>e</sup>	580	F/C	F
Na <sup>+</sup> (CE) <sup>f</sup>	581	S	S
K <sup>+</sup>	594	C	C
K <sup>+</sup> (CE) <sup>f</sup>	580	S	S
Cs <sup>+</sup>	590	C	C
Free <sup>g</sup>	580	F	F

<sup>a</sup> C = contact, S = separated, F = free.

<sup>b</sup> For reference, see Table 2.

<sup>c</sup> At concentrations from  $8 \times 10^{-5}$  M to  $5 \times 10^{-6}$  M, excited at 359 nm, or 540 nm.

<sup>d</sup> Independent of excitation wavelength, in the presence of hundred-fold excess of sodium tetraphenylborate.

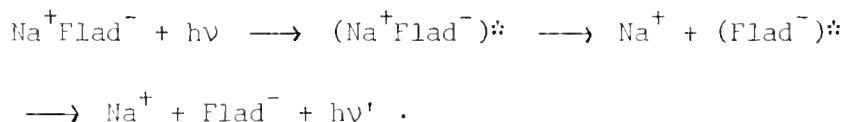
<sup>e</sup> Excited at 389, under same conditions as c.

<sup>f</sup> Slight excess of dicyclohexyl-18-crown-6 added.

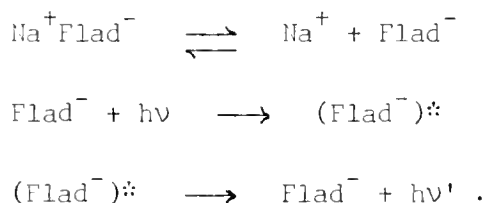
<sup>g</sup> Seen in all the above at low concentrations.

absorption maxima (550, 371, 359 nm), the sodium salt has a broad emission band, 580-600 nm, depending on concentration; as the concentration increases, the peak shifts toward 600 nm. If excited at 388 nm, where the solvent-separated ion pairs, or free ions, absorb, sodium fluoradenyl emits at 580 nm. Upon addition of a hundred-fold excess of sodium tetraphenylborate, the emission maximum shifts to 600 nm and becomes independent of excitation wavelength. This indicates that the species emitting at 580 nm is not a solvent-separated ion pair, but corresponds to the free ion.

There are two possible paths for the creation of excited free ions in this system. In the first, the contact pair, after excitation, dissociates into free ions:



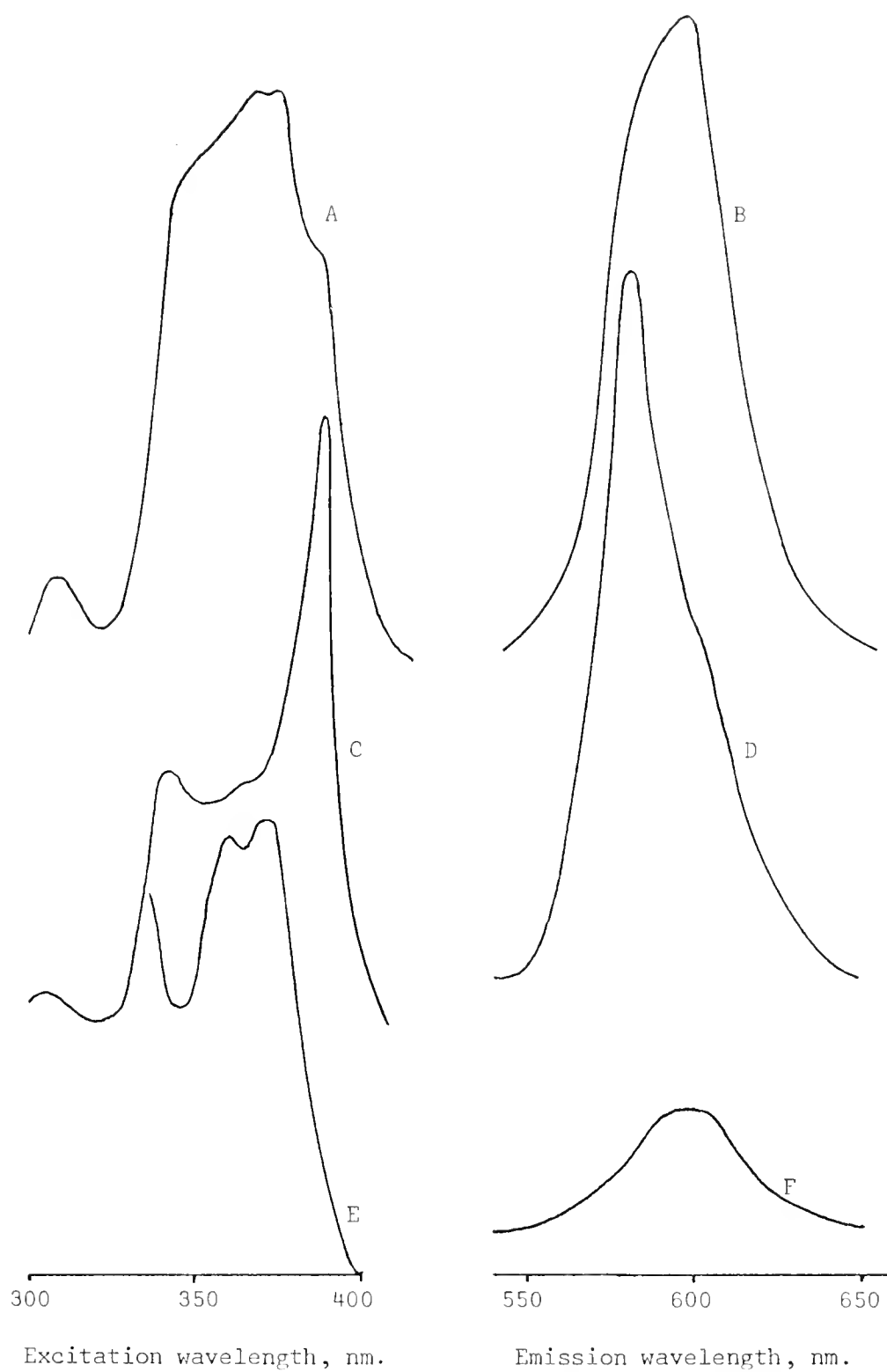
The second is simply excitation of the free ion, i.e.



Since addition of sodium ion causes not only changes in the emission spectrum, but also causes corresponding changes in the excitation spectrum, it must be concluded that no pathway which depends upon excitation of a single species can explain the behavior, which means that the first alternative must be discarded. See Figures 11 and 12 (Figure 12 is an absorption spectrum included for comparison).

Using the room temperature dissociation constant of the salt

Figure 11. Effect of common ion on excitation and emission spectrum of fluoradenyl sodium in THP;  $[\text{NaFlad}] = 5 \times 10^{-5} \text{M}$ .  
A.  $\lambda(\text{emission}) = 600 \text{ nm}$ ;  
B.  $\lambda(\text{excitation}) = 371 \text{ nm}$   
C.  $\lambda(\text{emission}) = 580 \text{ nm}$ ;  
D.  $\lambda(\text{excitation}) = 388 \text{ nm}$ ;  
E,F after addition of 1 equivalent  $\text{NaBph}_4$  independent of emission or excitation wavelength, respectively.



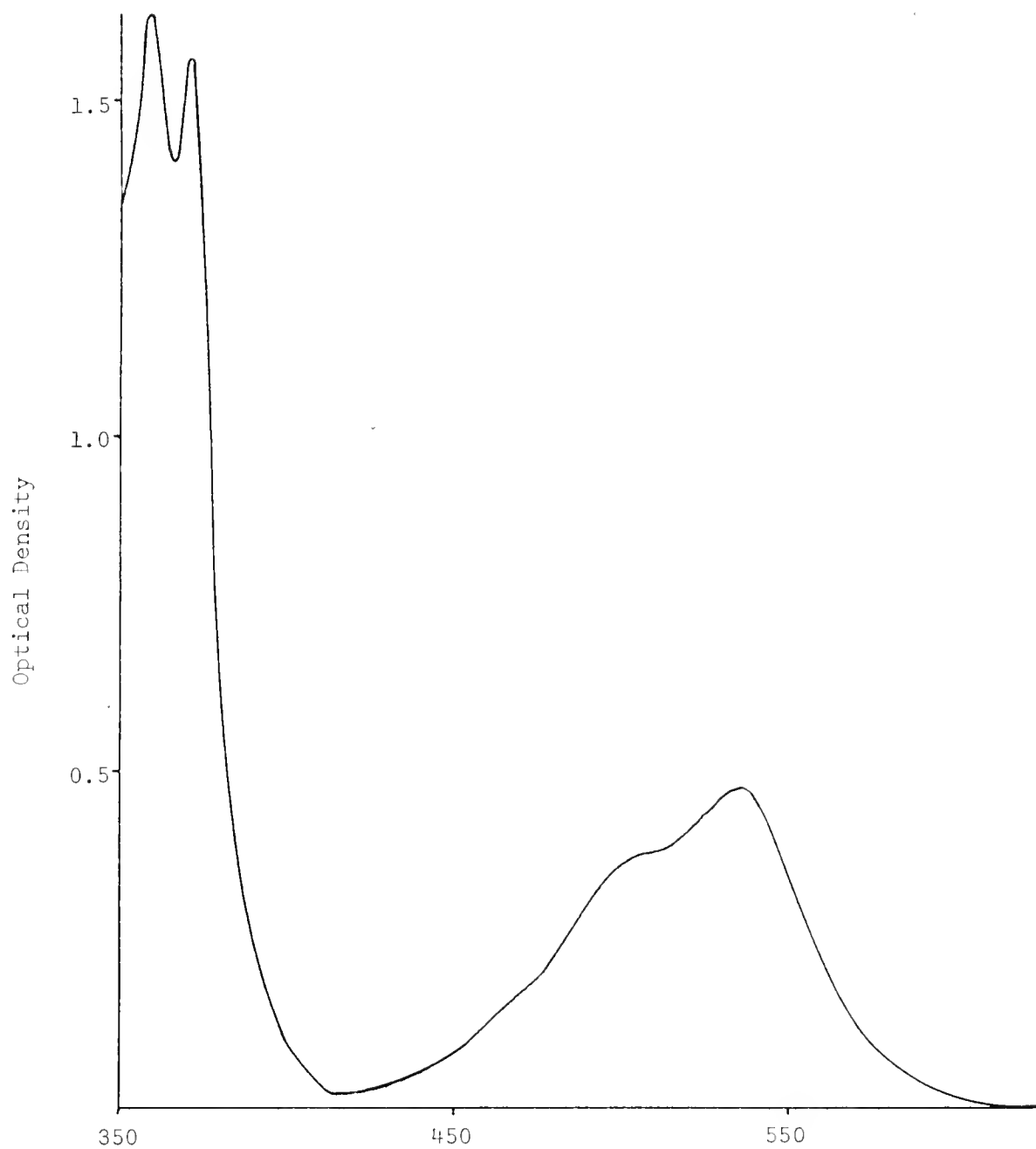


Figure 12. Absorption spectrum of fluoradenyl sodium in THP;  
[NaFlad] =  $1 \times 10^{-4} \text{M}$ .

in the ground state (obtained from preliminary conductance measurements in this laboratory, in which a value of 48 for the limiting conductance of fluoradenyl sodium in THP was used) of  $1.1 \times 10^{-8}$  mole/l, it was thought desirable to try to calculate a dissociation constant from the excitation spectrum of the salt at a known concentration to compare with the number obtained from conductance. Using the excitation spectrum of the salt at  $6.25 \times 10^{-6}$  M, comparing peak heights at 359 nm and 389 nm, subtracting the contributions of one species to the other's excitation maximum, and taking into account the differences in quantum yield (see below) a value,  $K_d = 2 \times 10^{-8}$  M was obtained in quite reasonable agreement with the value obtained from conductance. This method, admittedly used here very crudely, gives promise of being quite useful for salts with very low dissociation constants.

As in the fluorenyl systems, the cation has a large effect on the intensity and the lifetime of the emission of the fluoradenyl anion. As the data in Table 7 indicate, again cesium acts to quench the fluorescence more than does sodium, while the free ion emits most intensely and has the longest lifetime. Although the lifetime of the crown ether-separated pair was not obtained, its intensity is

Table 7. Effect of cation on the lifetime and intensity of fluorescence of the fluoradenyl anion.

Cation	Solvent	Lifetime (ns)	Intensity <sup>a</sup>
Cs <sup>+</sup>	THP	4.2	8
Na <sup>+</sup> <sup>b</sup>	THP	11.8	25
Free <sup>c</sup>	Acetonitrile	47.8	100

<sup>a</sup> In relative units.

<sup>b</sup> In the presence of a slight excess of sodium tetraphenylborate.

<sup>c</sup> Lithium as counterion.

roughly the same as that of the free ion. Again, as in the fluorenyl salts, the addition of crown ether has a striking effect, not only on the position of the emission maximum, but on its intensity.

#### Effect of Solvent and Hydrogen Bonding

In Table 8 are listed the salts and their emission maxima in different solvents. As opposed to fluorenyl systems, there is no evidence for charge transfer-type interactions in any of the systems examined.

A comparison of Tables 4 and 8 shows that, for the aprotic solvents, the same order of cation coordinating ability is obtained for the fluoradenyl salts as was found to hold for the fluorenyl salts.

Also, as in the fluorenyl systems, there is virtually no difference in position of the emission of the separated ion pair and that of the free ion. More remarkable, in view of the differences in charge distribution between the ground and excited states, there is virtually no effect of solvent polarity on the position of the emission maximum of the separated ion pair, or free ion, from THF (dielectric constant = 5.61) to acetonitrile (dielectric constant = 37.5).<sup>71</sup> (The same lack of a solvent effect is seen in the absorption spectrum of these salts.) This indicates either that both the ground and excited states of the anion are solvated to the same extent, or that neither is specifically solvated at all. Although this point will be more fully examined in the General Discussion, the redistribution of charge, indicated by Hückel calculations and invoked to help explain the cation dependence of both the absorption and the fluorescence

Table 8. Effect of solvent upon the ion pairing of excited alkali fluoradenyl salts, at  $1 \times 10^{-5} \text{M}$ .

Cation	Solvent	Emission Maximum (nm)	Type of Ion Pair <sup>a</sup>	
			Ground <sup>b</sup>	Excited
$\text{Li}^+$	Dioxane <sup>c,e</sup>	582, 595	C	C
	DME	581	S	S
	Acetonitrile	580	F	F
	THF	580	S	S
$\text{Na}^+$	THP <sup>d,e</sup>	600	C	C
	THF	580	50% C : 50% S	S
	n-PrNH <sub>2</sub>	583	80% C : 20% S	S
	3n-PrOH:7THP <sup>f</sup>	583	C, S-H	C,S
	t-BuOH <sup>f</sup>	588	C	C-F
	n-PrOH <sup>f</sup>	587	F-H	F-H
	EtOH <sup>f</sup>	586	F-H	F-H
	MeOH <sup>f</sup>	585	F-H	F-H
$\text{K}^+$	THP	594	C	C
$\text{Cs}^+$	THP	590	C	C
$\text{n-PrNH}_3^+$	n-PrNH <sub>2</sub>	582	S	S
$\text{Na}^+(\text{CE})^g$	THP	581	S	S
	THF	580	S	S
	3n-PrOH:7THP	581	S	S
	t-BuOH <sup>f</sup>	580	S	S
	n-PrOH <sup>f</sup>	587	F-H	F-H

<sup>a</sup> C = contact, S = separated, F = free, H = hydrogen bonded.

<sup>b</sup> See Table 2.

<sup>c</sup> Anomalous system, see text section on aggregation.

<sup>d</sup> In the presence of a large excess of sodium tetraphenylborate.

<sup>e</sup> Dependent on excitation wavelength.

<sup>f</sup> Broad peak, centered at position indicated.

<sup>g</sup> Slight excess of crown ether added.

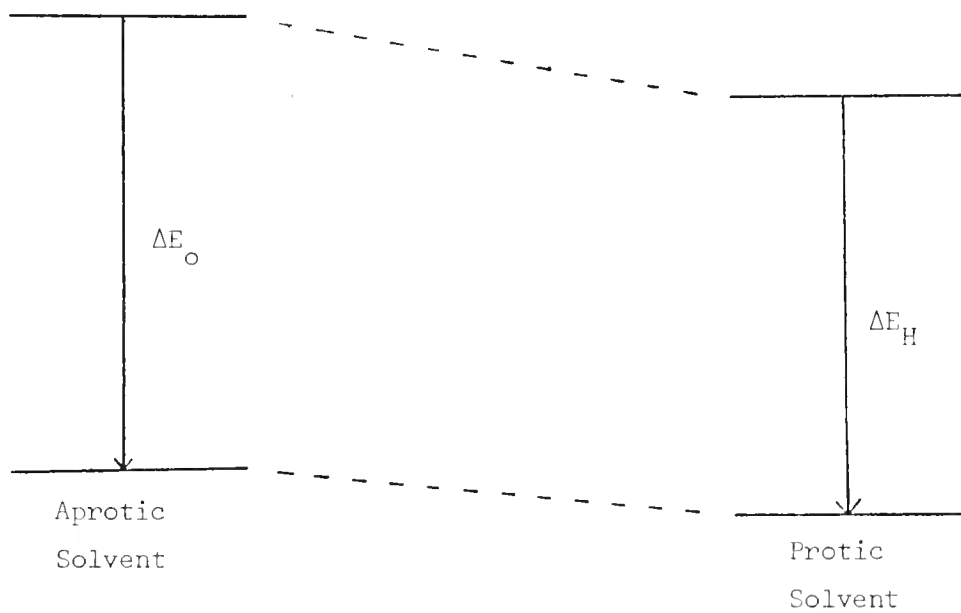
spectra, is inconsistent with any model invoking specific solvation of the anion, barring an accidental cancellation of effects.

In the protic solvents examined, there is a small red shift of the emission maximum of the free ion compared to the free ion in THP. That there is hydrogen bonding to the excited anion is indicated by the increase in peak width at half height ( $1170\text{ cm}^{-1}$  for the free ion in EtOH,  $650\text{ cm}^{-1}$  for the free ion in THP), the decrease in intensity (the free ion in THP emits approximately nine times more intensely than it does in the protic solvents), and the slight red shift in the position of the maximum.<sup>25-27,37,72</sup>

Also, the results in the THP-n-propanol system suggest that, as in the ground state,<sup>13</sup> the carbanion-alcohol hydrogen bond can be facilitated by the presence of the cation. In a  $1 \times 10^{-5}\text{ M}$  sodium fluoradenyl solution in 30 per cent n-propanol, 70 per cent THP, the carbanion emits at 587 nm. Addition of crown ether shifts the emission maximum to 581 nm. Dilution to about  $1 \times 10^{-6}\text{ M}$  causes the emission maximum to shift back to 586 nm.

The shift of the emission spectrum relative to the aprotic solvents can be explained by an argument analogous to that used to explain the effect of cation. The hydrogen bond formed to the excited anion is not the same as that to the ground state anion. Assuming that the solvent has time to rearrange and reach its equilibrium position to the excited anion within the lifetime of the excited state, the hydrogen bond formed should stabilize the excited anion more than the ground state anion which it will become immediately following emission (the Franck-Condon ground

state anion), i.e. the energy difference between the excited and ground state free ion in a protic solvent will be less than that for the free ion in an aprotic solvent. See Figure 13.



$$\Delta E_o > \Delta E_H$$

$\therefore$  Hydrogen bonding causes a red shift,  
in the fluorescence spectrum.

Figure 13. Effect of hydrogen bonding on the fluorescence of the free fluoradenyl anion.

### The Radical Anion of Anthracene: Results and Discussion

To determine how applicable the concept of ion-pairing was to the excited state of radical systems, the sodium and cesium salts of the anthracenide radical anion were prepared as previously described in Chapter II.

A typical absorption spectrum of the sodium salt in THF is given in Figure 14. This agrees well with other published spectra of these salts.<sup>44-48</sup> As in the other systems investigated, these salts are known to exhibit ion-pairing in the ground state. The rationale of the position of the absorption peaks exactly parallels that of the other systems.

Since the MPF-2A allows excitation only at wavelengths below 700 nm, in looking at the excitation spectra of these salts, it was found that the peaks corresponded to those of anthracene. Since there was always unreacted hydrocarbon in the solution, its presence is not surprising. However, that the excitation spectra of the salt correspond to those of the hydrocarbon is not a trivial result because it shows a significant avenue of energy transfer in these systems.

A typical fluorescence spectrum contained a single peak near the end of the instrument's wavelength range for emission. The results for all the salts studied are compiled in Table 9. The fluorescence spectrum of the sodium salt in THF at  $1 \times 10^{-4}$  M has a peak at 773 nm which shifts to 760 nm on dilution to  $1 \times 10^{-5}$  M while increasing in intensity. Further dilution leaves this peak position unchanged. The spectrum at  $1 \times 10^{-4}$  M could either be due to the equilibrium between tight and loose pairs (as in fluorenyl sodium

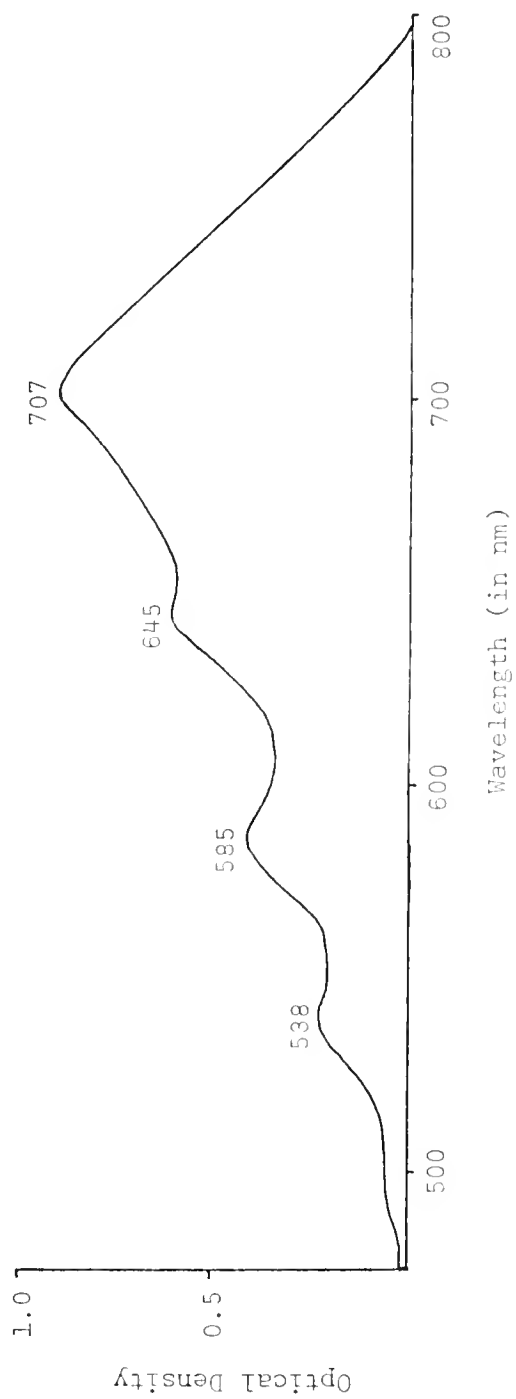


Figure 14. Absorption spectrum of sodium anthracenide in THP.  $[\text{Na}^+\text{Anth}^-] \approx 1 \times 10^{-4} \text{ M}$ .

in THF) or be due to ionization, since the dissociation constant is fairly high ( $4 \times 10^{-6}$  M).<sup>73</sup> Since the absorption band is extremely broad, the extinction coefficient, even at 760 nm, is quite high ( $\epsilon_{760} \approx 3000$ ). This would indicate that the peak at 773 nm was due to either separated ion pairs or free ions, but shifted by reabsorption effects. This is even more likely since the sodium salt, in THP, where neither free ions nor separated ion pairs would be expected, has no observable emission, until very low concentrations ( $< 8 \times 10^{-6}$  M).

Table 9. Ion-pairing in the ground and excited states of alkali metal-anthracenide salts.

Cation/solvent	Absorption maximum (nm)	Fluorescence maximum (nm)	Ion Pair <sup>a</sup>
Na <sup>+</sup> /THP or THF	707	>770	C
Na <sup>+</sup> /THP + glyme-5 <sup>b</sup>	750	760	S
Cs <sup>+</sup> /THF	725	768	C
Free ion <sup>c</sup> /THF	750	759	F

<sup>a</sup> C = contact, S = separated, F = free ion.

<sup>b</sup> Glyme-5 25 per cent by volume, complexing agent for cations; see text.

<sup>c</sup> Seen in solutions of Na<sup>+</sup> or Cs<sup>+</sup>Anth<sup>-</sup>.

Crown ethers were not used as complexing agents because it was feared that they might react with the radical anions.<sup>74</sup> Instead, glyme-5 ( $\text{CH}_3\text{O}[\text{CH}_2\text{CH}_2\text{O}]_4\text{CH}_3$ ), a straight chain analog of 18-crown-6, was used to complex the cation. As can be seen from the table, as for the other systems studied, the separated and free ion have the same fluorescence maximum. Also, again the free ion emits approximately an order of magnitude more intensely than does the cesium contact ion pair.

#### CHAPTER IV ATTEMPTS TO GENERATE CARBANIONS FROM EXCITED HYDROCARBONS

In the ground state,<sup>75</sup> fluorene has an acid dissociation constant of about  $10^{-23}$ . However, based on Förster cycle calculations,<sup>66,76</sup> its first excited state is estimated to be about 29 orders of magnitude more acidic than in the ground state.

Fluoradene, in the ground state, shows a rather striking dependence of its pKa on the solvent. In methanol,<sup>77</sup> the pKa is 18.2; in dimethylsulfoxide,<sup>78</sup> the pKa is 10.5. The Förster cycle method indicates the excited hydrocarbon to be about 27 orders of magnitude more acidic than in the ground state.

In view of the great acidity of the hydrocarbons in the excited state, as indicated by Förster cycle calculations, several attempts were made to generate the excited state carbanion, especially in protic media. These attempts were unsuccessful, but some of the factors involved may help elucidate some of the data for the fluoradene-fluoradenyl system.

Solutions of fluorene and fluoradene were prepared under vacuum, with purified, degassed, solvents. To these solutions were added known amounts of base via evacuated ampoules. Absorption and fluorescence spectra were taken as before.

In Figures 15 and 16 are absorption spectra of fluorene and fluoradene in various media. In Figures 17 and 18 are emission spectra of fluorene and fluoradene in various media.

As can be seen from the figures, fluorene is surprisingly

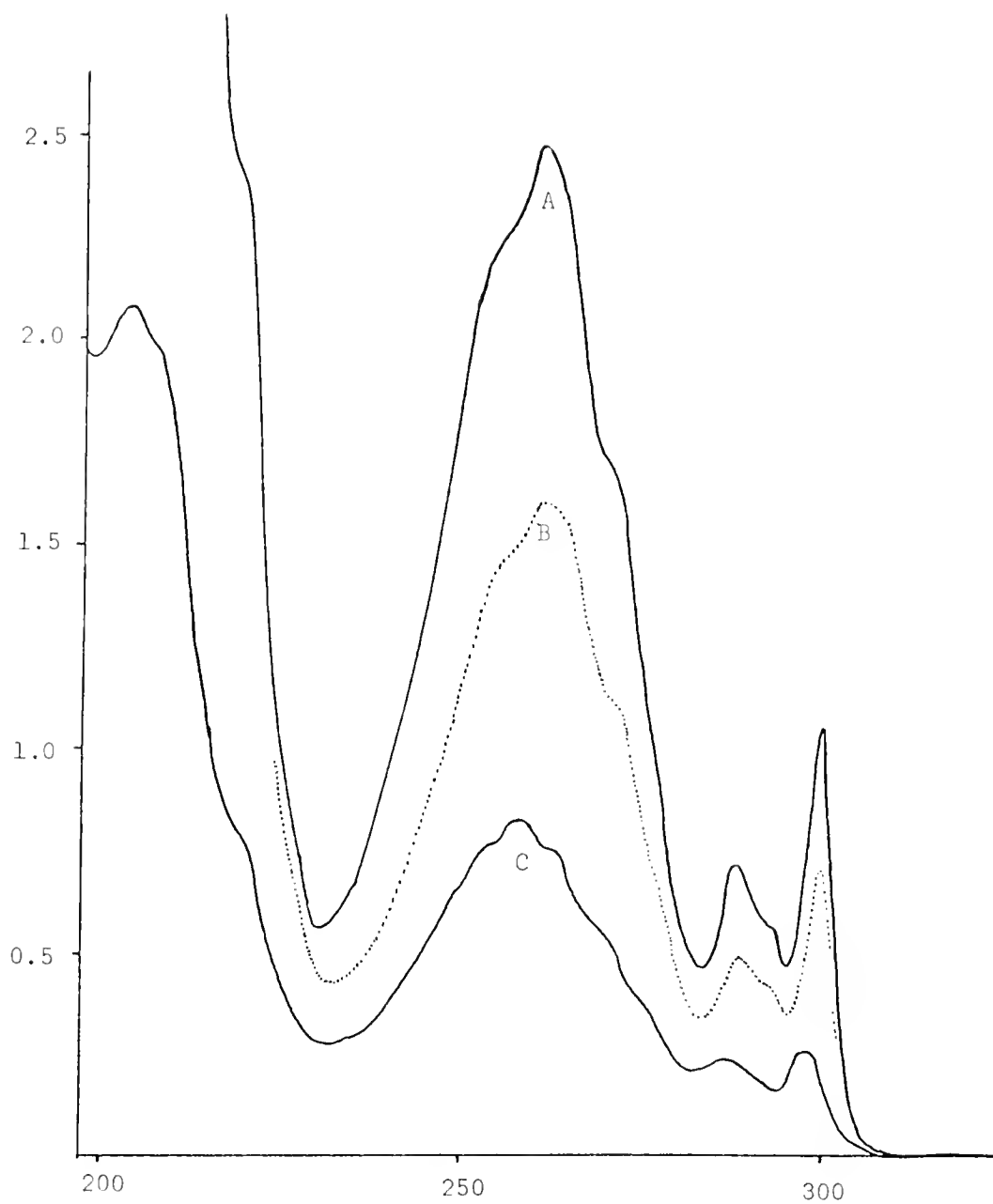


Figure 15. Absorption spectra of fluorene in various solvents;  
A. Hexane; B. Methanol; C. Water.

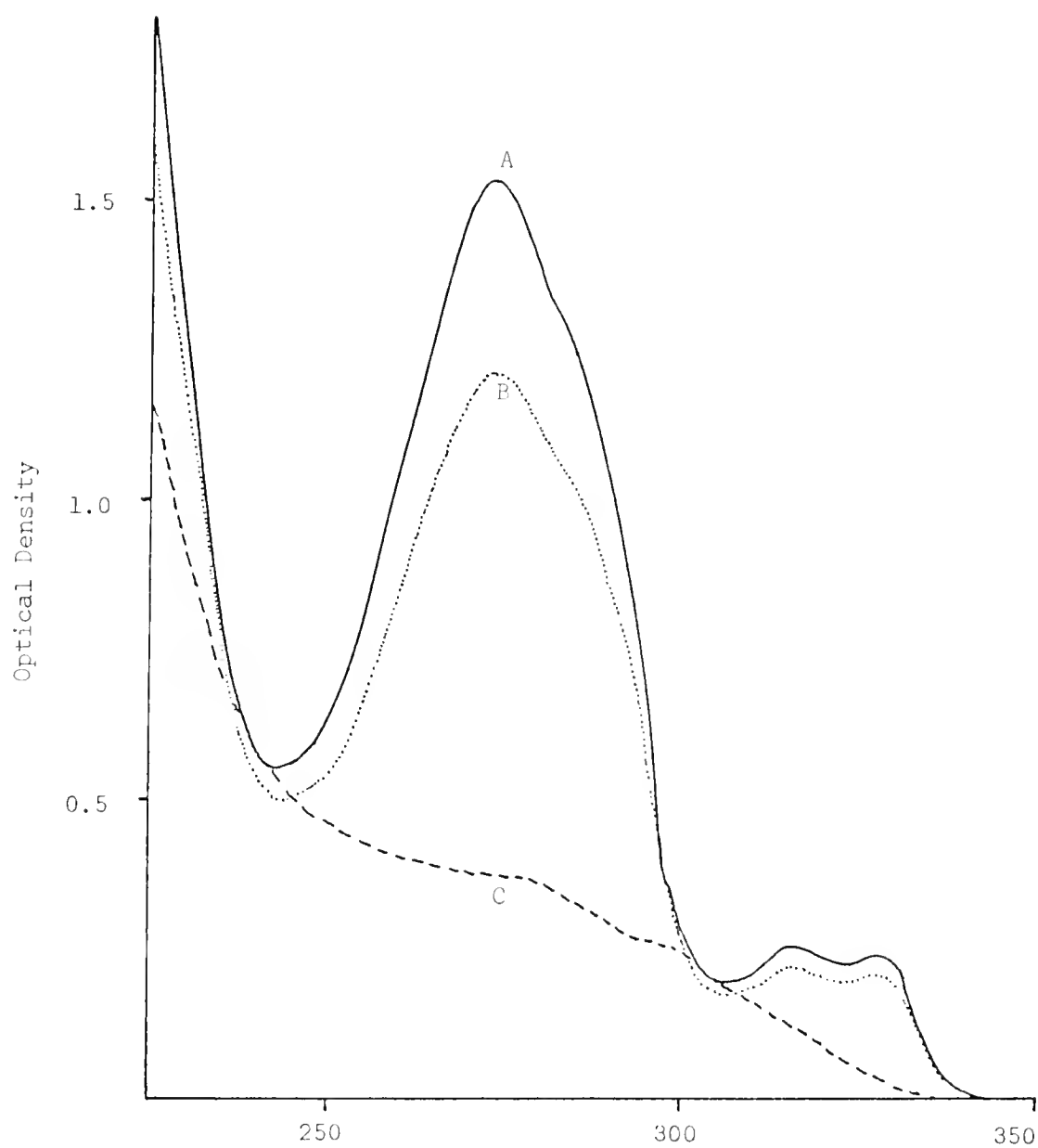


Figure 16. Absorption spectra of fluoradene in various solvents; A. Hexane; B. Ethanol; C. Water.

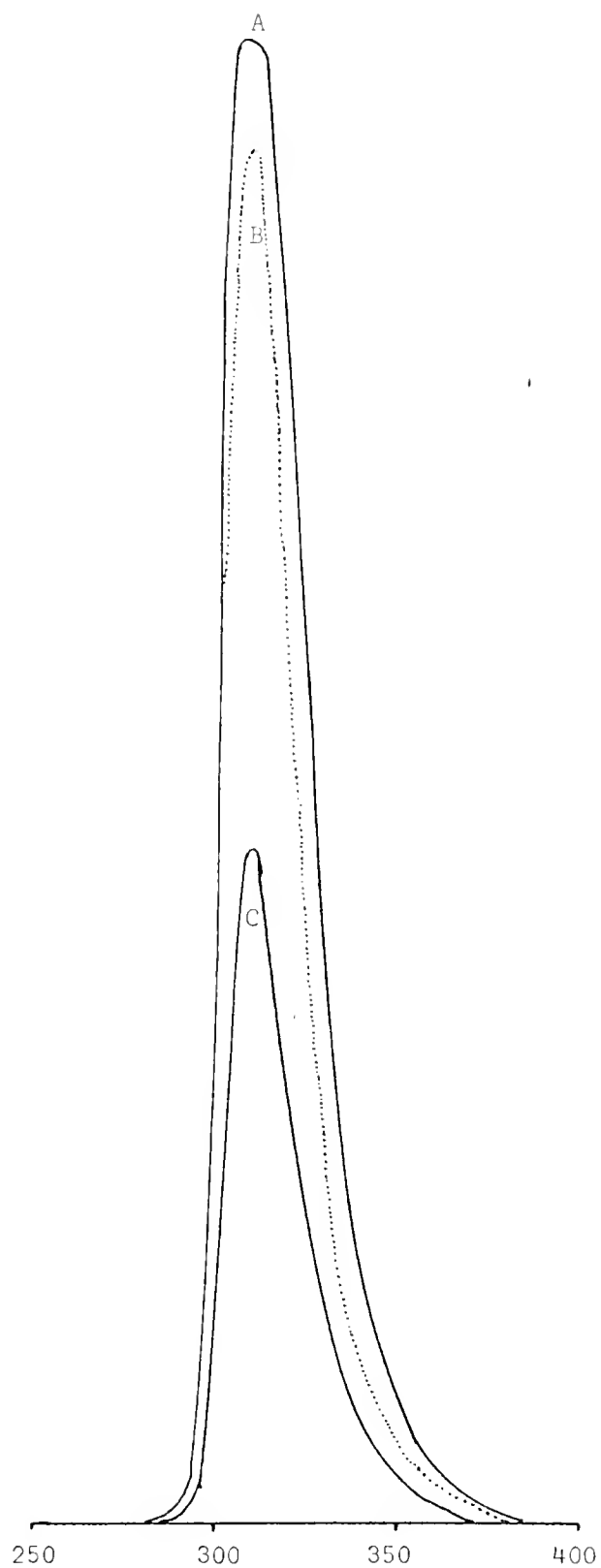


Figure 17. Fluorescence spectra of fluorene in various solvents; A. Water; B. Methanol; C. Hexane.

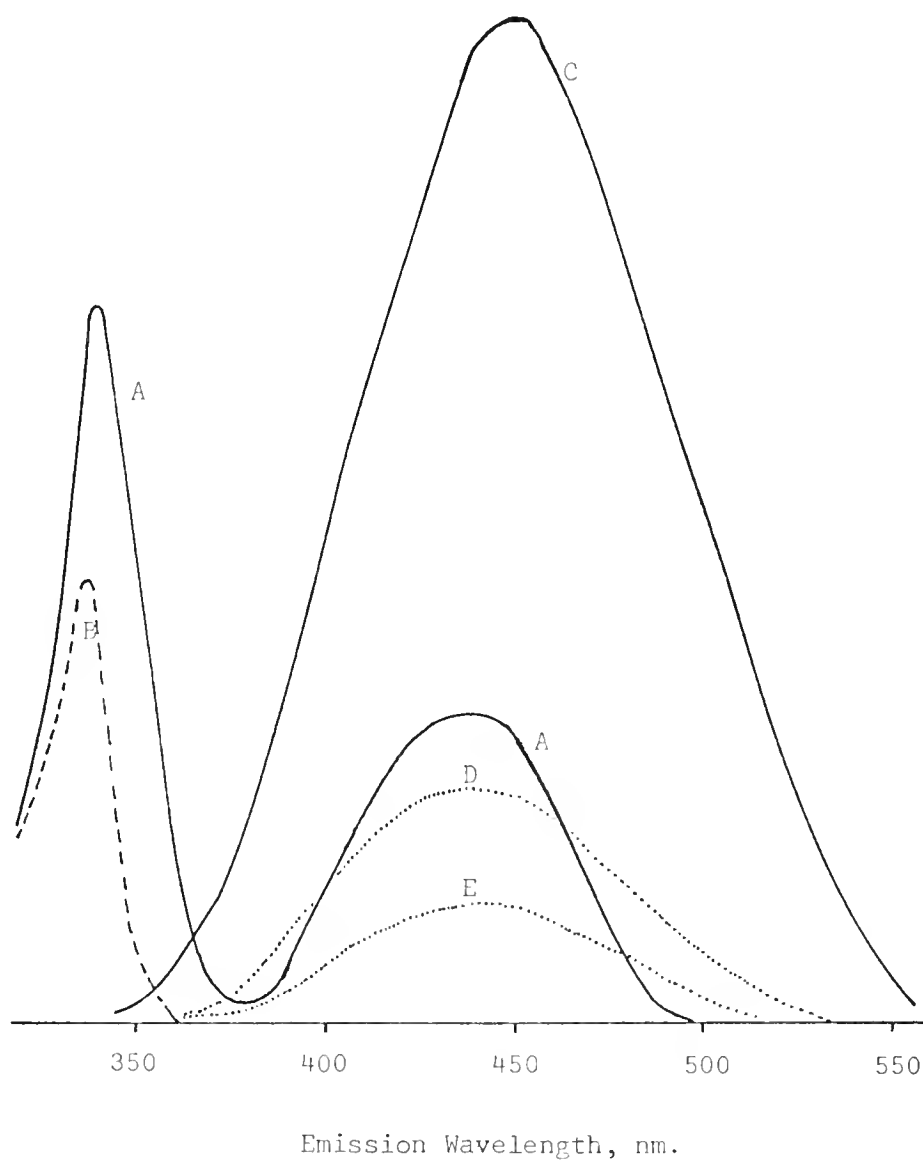


Figure 18. Emission spectra of fluoradene in various media. A. Hexane,  $1 \times 10^{-4} \text{M}$ ; B. Hexane,  $1 \times 10^{-5} \text{M}$ ; C. Methanol,  $1 \times 10^{-5} \text{M}$ ; D. Hexane,  $5 \times 10^{-2} \text{M}$ ; E. Ethanol,  $4 \times 10^{-6} \text{M}$  (not to scale).

soluble in the protic solvents, roughly  $10^{-4}$  M. At the same time, fluoradene is almost completely insoluble in water, though not in other protic solvents.

Figure 18 shows that, in the protic solvents, fluoradene emits from an excimer state exclusively, while in hexane this excimer emission is seen only at higher concentrations. As is shown in Appendix 3, this is a good indication of aggregation in the fluoradene-protic solvents systems.

Addition of base to fluorene in the protic solvents and irradiation gave no sign of fluorescence from the anion. Since the emission of the anion could still be seen at  $10^{-8}$  M, if present, it must be concluded that the concentration of the excited anion is less than this.

Additions of base to fluoradene solutions were somewhat more successful in producing anion. The anion did not appear at all in water, or in a mixture of water and 5% ethanol, when base was added, but titrations in methanol and ethanol did produce anion, but not until H values of about 16; yielding a pKa of 18, consistent with literature values.<sup>77</sup>

From the above, one must conclude that while, thermodynamically, the equilibrium between excited hydrocarbon and excited anion lies far on the side of the excited anion, there are other factors which make attainment of this equilibrium nearly impossible.

(1) As pointed out by Mason and Smith,<sup>79-81</sup> the rate of ionization of the excited state carbon acids in protic solvents is probably limited by the amount of reorganization required by the solvent. The extensive network of hydrogen bonds in a solvent such as water, around a hydrophobic species, requiring a considerable expenditure

of energy in order to reorient itself to accomodate a proton and an anion.

(2) In fluoradene, the possibility of excimer formation would significantly decrease the amount of "free" excited monomer available to react with base.

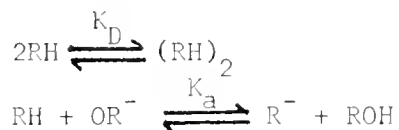
(3) Ground state aggregation of the hydrocarbons, especially in protic solvents, could hamper diffusion of base to the active site of the carbon acid.

(4) The intensity of the exciting light would determine the concentration of the excited hydrocarbon, and, hence, of the excited carbanion. The relatively weak source of a commercial instrument would not produce too high concentration of excited carbanion.

(5) Lastly, the breaking of a carbon-hydrogen bond is involved, which would probably require a large energy of activation.

It was not unexpected that the attempts to generate carbanions from their excited hydrocarbons failed; however, the information obtained from these experiments points to a previously ignored factor which might account for the tremendous difference in the pKa of fluoradene in methanol and DMSO: aggregation of the hydrocarbon in methanol.

If one considers only a hydrocarbon dimerization reaction, in addition to the carbon acid dissociation in alcohol, then:



where RH is the hydrocarbon acid,  $\text{R}^-$  its conjugate base, and ROH/OR $^-$  are the alcohol and alkoxide, respectively. Then, assuming that most of the hydrocarbon is aggregated, i.e.  $[(\text{RH})_2] \gg [\text{RH}] + [\text{R}^-]$ ,

it follows that  $[(\text{Rh})_2] \approx C_o/2$ ,  $C_o$  the initial amount of hydrocarbon present. Thus,

$$(1) \quad K_a = \frac{[\text{R}^-]}{[\text{RH}][\text{OR}^-]} ; \quad K_D = \frac{[(\text{RH})_2]}{[\text{RH}]^2}$$

$$(2) \quad K_a = \frac{[\text{R}^-]}{[\text{OR}^-]} \left( \frac{2K_D}{C_o} \right)^{1/2}.$$

Substituting (2) into (1) yields  $K_D = C_o/(2[\text{RH}]^2)$ . Since, in methanol, no monomeric fluoradene could be detected, one must conclude that  $[\text{RH}] < 1 \times 10^{-7} \text{ M}$  (a conservative estimate for the least amount of monomer detectable). Thus with  $C_o = 1 \times 10^{-5} \text{ M}$ , it follows that  $K_D > 5 \times 10^{18}$ , indicating that virtually all the fluoradene is aggregated in methanol. So far, no assumptions are made about the pKa values.

Now, suppose there is no difference in the pKa of the hydrocarbon monomer in DMSO or methanol, but that the aggregated form is virtually inert to base. Thus, the pKa of fluoradene in methanol is actually an apparent value,  $\text{pKa}^{\text{app}}$ . From (2),  $K_a^{\text{app}} \equiv \frac{[\text{R}^-]}{[\text{OR}^-]C_o} = \frac{K_a}{(2K_D C_o)^{1/2}}$

or,  $\text{pKa}^{\text{app}} = \text{pKa} + 1/2 \log 2 + 1/2 \log (K_D C_o)$ .

If  $K_D > 5 \times 10^{18}$ ,  $C_o = 1 \times 10^{-5} \text{ M}$ , then  $\text{pKa}^{\text{app}} > \text{pKa} + 7$ , or, since pKa in DMSO is 10.5,  $\text{pKa}^{\text{app}}$  in methanol  $> 17.5$ .

Thus, aggregation of the hydrocarbon in protic solvents may be quite a significant factor in the apparent solvent dependence of the acid dissociation constant.

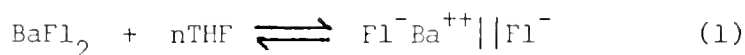
CHAPTER V  
AGGREGATION EFFECTS ON CARBANION FLUORESCENCE

Earlier, it was proposed that in order to understand aggregated systems, the barium salts would serve as good models. This is due to several factors. First, in the fluorenyl systems which are actually aggregated in the sense of forming n-mers (such as lithium fluorenyl in toluene or dioxane), the only information available is the average value of n in solution, obtained from kinetic experiments.<sup>39,82</sup> In the barium fluorenyl systems, one can focus on the anion dimer (with respect to the anion). Also, the barium fluorenyl system has the significant advantage of having an absorption band reasonably isolated from others, which is not true of the barium fluoradenyl salt.

However, there are certain anomalies to the barium fluorenyl salt which must be borne in mind in applying results from this system to others. The size of the barium cation is roughly that of the potassium ion (1.35 Å for  $\text{Ba}^{++}$ , 1.33 Å for  $\text{K}^+$ ), but the charge/radius ratio is nearly that of lithium (1.48 for  $\text{Ba}^{++}$ , 1.67 for  $\text{Li}^+$ ). Thus, while certain anomalies of lithium fluorenyl which have been ascribed solely to its small size<sup>83,84</sup> may not be elucidated by data for the barium system, the large electrostatic field of the barium cation, or more particularly of fluorenyl<sup>-</sup> $\text{Ba}^{++}$ , compared to sodium fluorenyl, as felt by another fluorenyl anion, may cause "collapse" of the aggregate which would not occur for other systems.

A more significant problem is the temperature dependence of

the absorption spectrum of bisfluorenyl barium in THF (the room temperature spectrum is shown in Figure 19). There is little qualitative change in the spectrum from 25° to -70° C; even at the lower temperature, there are only about 20% separated ion pairs. As the temperature is decreased still further, there is a dramatic increase in the peak at 372 nm, due to the shift of equilibrium (1) to the right as the temperature is lowered. At -100° C, the salt is virtually all in the separated form.<sup>85</sup>



This is in striking contrast to the behavior of sodium fluorenyl in THF, which has a similar absorption spectrum at room temperature, but which shows a regular increase in the 372 nm peak as the temperature is decreased, indicating a regular increase in the amount of separated pairs present. This contrast calls into question the nature of the 372 nm peak in the absorption spectrum of bisfluorenyl barium in THF at room temperature.

Thermodynamic data on the bisfluorenyl strontium salt,<sup>42</sup> a similar system, show  $\Delta H$  and  $\Delta S$  for (1) to be  $-12.3 \pm 2$  kcal/mole and  $-47 \pm 7$  entropy units, respectively. Assuming that  $\Delta H$  for the barium salt is not too different from that of the strontium salt ( $\Delta H$  for lithium fluorenyl is about the same as  $\Delta H$  of sodium fluorenyl, in THF<sup>39</sup>), one finds that:

$$\log \frac{K_{300}}{K_{200}} = \frac{\Delta H}{4.58} \left( \frac{1}{200} - \frac{1}{300} \right) \quad (2)$$

If  $\Delta H \approx -12.3$  kcal/mole,  $K_{200} \approx 4$ , then (2) implies that  $K_{300} \approx 1.10^{-5}$ , i.e. there are only about 0.001% separated ion pairs in the

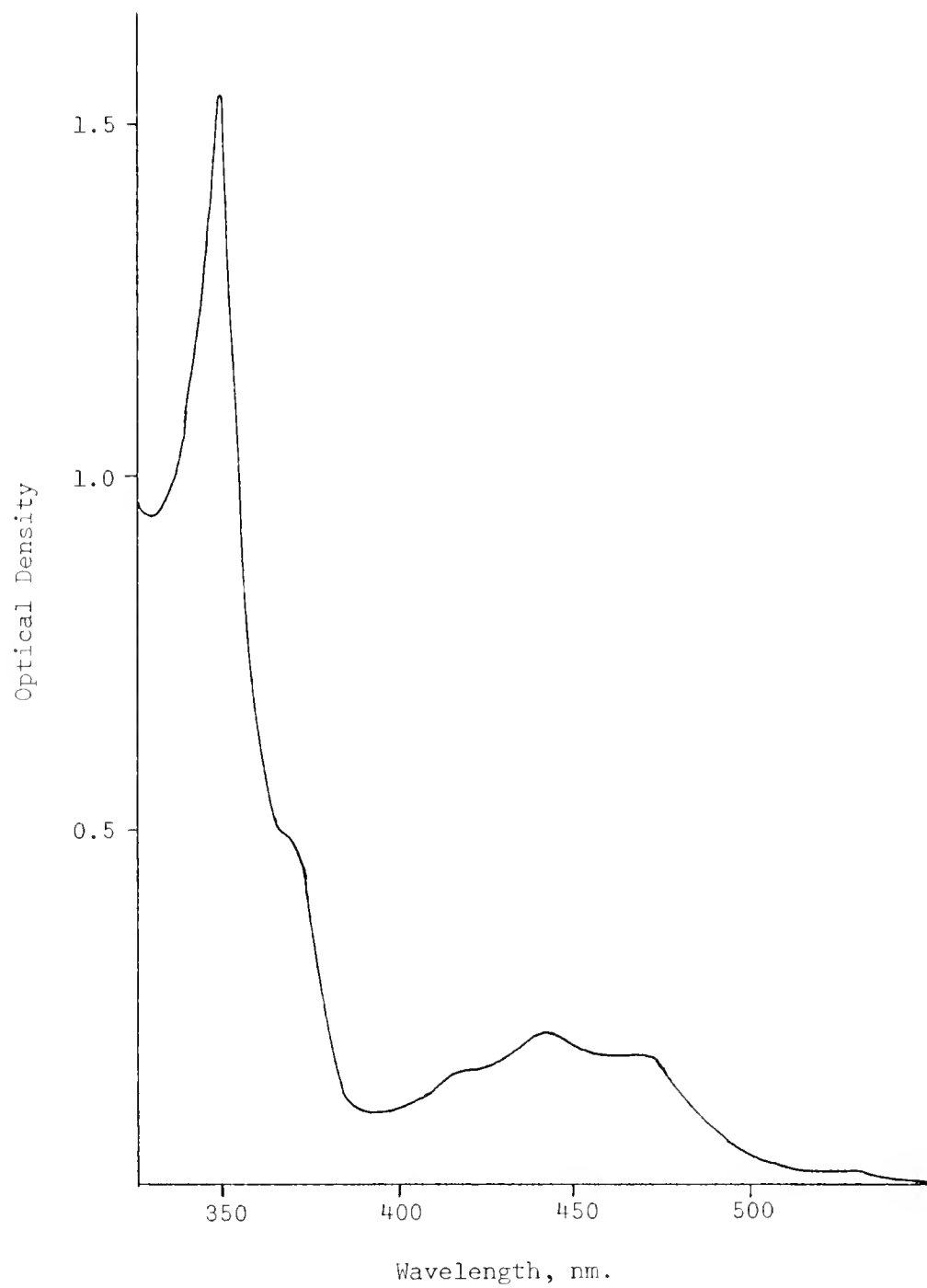


Figure 19. Absorption spectrum of bisfluorenylbarium in THF.

bisfluorenyl barium in THF solution at room temperature. Thus, on thermodynamic grounds, one is led to doubt that the absorption peak at 372 nm, for this system, is due to separated pairs.

The absorption spectrum of the salt in THP at room temperature, which also has a shoulder at 372 nm, gives further evidence that this peak is not due to separated ion pairs. Given the much greater cation solvating ability of THF compared to THP, this makes it very likely that the 372 nm peak in both solvents is primarily due to some other effect than equilibrium (1).

Another effect one would hope to be able to explain is the severe hypochromism of this system. As noted by Smid,<sup>43</sup> the linear extinction coefficient of the 347 nm band is 7300, compared to a value of 11,000 to 12,000 for contact alkali metal salts in THF.

The fluorescence and excitation spectra of the salt in THF and THP are very instructive (see Figures 20 - 22 and Table 10). The

Table 10. Fluorescence of barium fluorenyl in THF and THP, at  $1 \times 10^{-5} M$ .

Solvent	Excitation wavelength	Emission wavelength maximum	Type ion pair
THP	All absorbing wavelengths	568 nm	contact-"aggregate"
THF	373 nm 347 nm	528 nm $\approx 530, \approx 570$ nm	separated separated; contact-"aggregate"
THF + 20% CE <sup>a</sup>	347 nm 373 nm	533 nm 528 nm	mainly separated separated

<sup>a</sup> [dicyclohexyl-18-crown-6]  $\approx 0.20$  [Ba<sup>++</sup>].

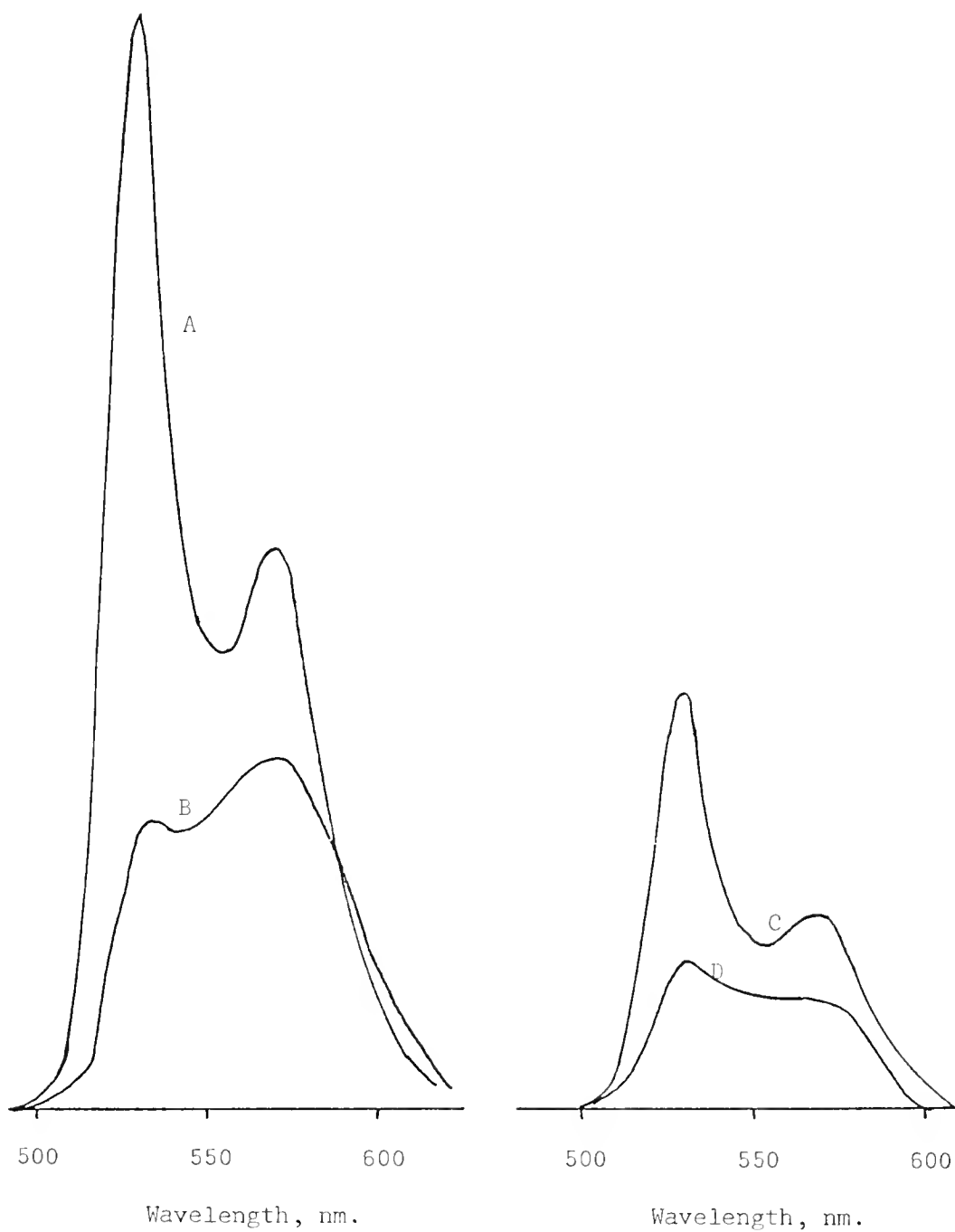


Figure 20. Emission spectra of bisfluorenylbarium in THF, as a function of exciting wavelength. A,B  $[Fl^-] = 1 \times 10^{-5} M$ ; C,D  $[Fl^-] = 3 \times 10^{-6} M$ ; A,C excited at 373 nm; B,D excited at 347 nm.

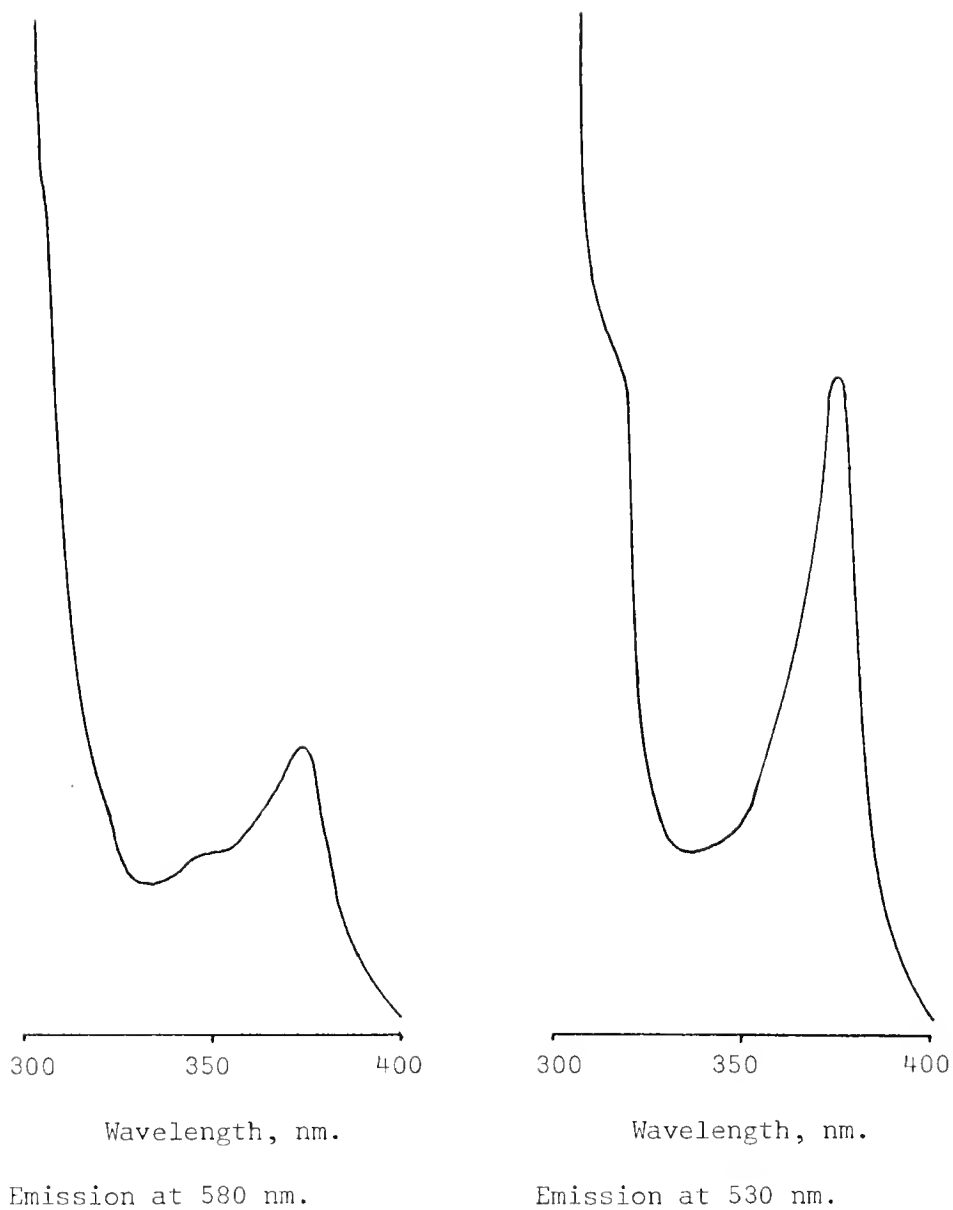


Figure 21. Excitation Spectrum of bisfluorenyl barium in THF as a function of emitting wavelength; total fluorenyl concentration =  $3 \times 10^{-6} \text{M}$ .

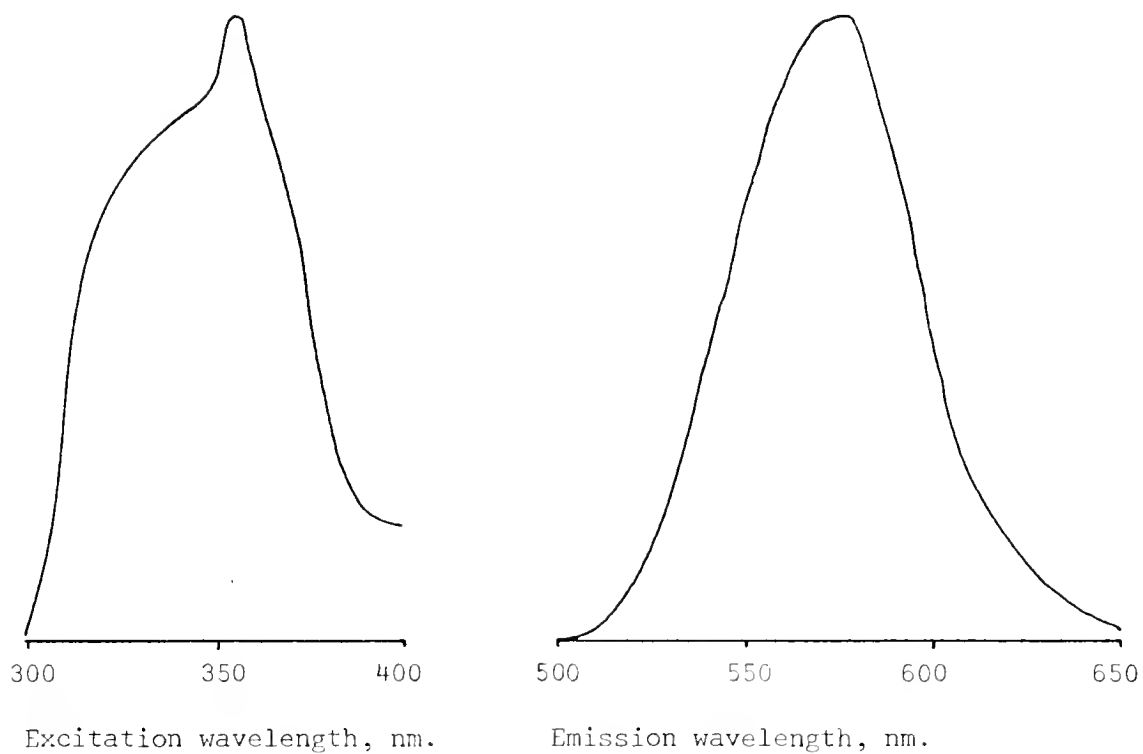


Figure 22. Excitation and emission spectrum of bisfluorenyl barium in THP; total fluorenyl concentration =  $1 \times 10^{-4} \text{M}$ .

spectrum in THF has peaks at 528 and 568, if excited at 373 nm, identical to those of the separated ion pair, or free ion. However, if excited at 347 nm, the intensity of the peak at 568 nm increases relative to the lower wavelength peak, indicating that there are two species present.

As has already been shown, it is highly unlikely that there is any significant amount of separated ion pairs in bisfluorenyl barium in THF. This implies that the species excited at 373 nm is the free ion. As a check of this, the emission of fluorenyl sodium in THF was compared to that of the barium salt, when both were at the same anion concentration ( $3 \times 10^{-6}$  M), and excited at the same wavelength. Under these conditions, the barium salt should have approximately 3% free ions ( $K_d = 3 \times 10^{-9}$  l/mol), while the sodium salt should have 33% free ions ( $K_d = 6 \times 10^{-7}$  l/mol). The relative intensities at 528 nm are 11:1, in striking agreement with the assumption that the species excited at 373 nm is the free ion.

The fluorescence of the other emitting species, excited at 347 nm, is better seen in THP, where this other species, the contact-"aggregate" is the only species present. This is to be expected, since the dissociation constant of the barium salt in THP should be significantly lower than in THF. The intensity of the emission from this contact-"aggregate" is extremely low; in fact, about thirty times lower than that of the free ion at the same wavelength (568 nm), and 75 times less than the intensity at the free ion maximum, indicating a great deal of self-quenching by the contact-"aggregate".

The excitation spectrum of the emitting species in THP is rather interesting, since it contains a peak around 355 nm. This peak has

no counterpart in the absorption spectrum, and its nature is unclear. It will be discussed in somewhat greater detail in the General Discussion.

Addition of about 25% crown ether to bisfluorenyl barium in THF had two effects. First, it increased the intensity of the peak at 528 nm (excited at 373 nm) by a factor of about ten (at  $4 \times 10^{-5}$  M). Secondly, there is an increase in the intensity of the emission from the other species, but it is much more modest, and mostly obscured by the free ion or separated ion pair spectrum. However, if the salt is excited at 347 nm, emission occurs at 533 and 568 nm, with a larger peak at 568 nm than for a pure separated ion pair. If one subtracts the contribution of the separated ion pair from this spectrum, one obtains the spectrum of a species emitting around 540 nm, presumably the contact cation,  $\text{Fl}^-\text{Ba}^{++}$ , which would emit about 30% as intensely as the separated pair. This is not seen in the uncomplexed case, as will be discussed in the General Discussion.

The low intensity of the salt's emission is probably due to two effects. First, the barium cation, being isoelectronic to the cesium ion, should cause reduced intensity, due to a heavy atom effect. The greater charge-to-radius ratio of barium would be expected to cause an accentuated effect, however, by forming a tighter ion pair, increasing the interaction between the cation and anion, thus causing greater quenching.

A second mechanism of quenching is specifically due to aggregation, the so-called exciton interaction, which Simpson,<sup>1</sup> and co-workers, and Kasha,<sup>6-8</sup> and coworkers, have applied to dyes and nucleotides.

In the following discussion, the basic relations of the theory of molecular excitons will be set down as they apply specifically to the dimer case, in the manner of Kasha.<sup>8</sup> It is assumed that intermolecular overlap between the two species is small, but finite, so that the monomer units preserve their individuality and the aggregate wave-functions and energies may be obtained by applying perturbation theory to the monomer. Denoting the two molecules in the dimer (in this case, fluorenyl anions) by A and B, the splitting of the monomer band due to exchange of excitation energy between A and B,  $\Delta E$ , is given by:

$$\Delta E = \frac{2\bar{M}_A \cdot \bar{M}_B}{R^3} - \frac{6(\bar{M}_A \cdot \bar{R})(\bar{M}_B \cdot \bar{R})}{R^5}$$

where  $\bar{M}_A$  and  $\bar{M}_B$  are the vector transition dipoles (such that  $|\bar{M}_A|^2 = |\bar{M}_B|^2 = |\bar{M}|^2$ ,  $\bar{M}$  the transition moment for the monomer), and  $\bar{R}$  is a position vector from the center of  $\bar{M}_A$  to the center of  $\bar{M}_B$ , i.e.  $R$  is the distance between the transition moment vectors of the two monomer units. This simplifies to  $E = \frac{2|\bar{M}|^2}{R^3} G$ , where  $G$  is a factor depending on the geometry of the aggregate. Further, the intensity of the transition from the ground state to the exciton states is proportional to the vector sum of  $\bar{M}_A$  and  $\bar{M}_B$ . Thus, while the exciton splitting will always occur, only one transition need be seen because the vector summation constitutes a sort of selection rule.

The mechanism of quenching is thus due to a lowering of the energy difference between the excited singlet and its associated triplet state, enhancing the rate of intersystem crossing, since the rate of intersystem crossing is proportional to the reciprocal

of this energy difference. Hence, the enhancement of phosphorescence usually observed in such systems, and the accompanying quenching of fluorescence come from the same cause.

If one assumes the geometry of the barium fluorenyl salt to be that of Smid and Hogen Esch, but allows the two essentially planar anions to tilt toward one another (x-ray patterns of similar fluorenyl salts assume this pattern),<sup>83,84</sup> then the exciton model predicts two bands, such that the oscillator strength of the first band, divided



by the oscillator strength of the second is equal to the square of the tangent of the angle between  $\bar{M}_A$  (or  $\bar{M}_B$ ) and the position vector  $\bar{R}$ , i.e.  $\frac{f_L}{f_H} = \tan^2 \alpha$ , where  $f_L$ ,  $f_H$  are the oscillator strengths for the low and high wavelength exciton bands, respectively, and  $\alpha$  is indicated in the figure.

In order to determine the oscillator strengths of the separate bands, plots of  $\epsilon(\tilde{\nu})$ , the decadic molar extinction coefficient (in  $\text{l}\cdot\text{mole}^{-1}\cdot\text{cm}^{-1}$ ), as a function of  $\tilde{\nu}$ , wave number (in  $\text{cm}^{-1}$ ), had to be made by converting the absorption spectrum of the dimer from wavelength to wave number. The areas of these plots were measured by a planimeter, and the ratio  $f_L/f_H$  derived from the ratio of the two areas. For bisfluorenylbarium in THP this ratio was 18.67, making angle  $\alpha \approx 77^\circ$ ; for THF,  $\alpha \approx 61^\circ$ .

This result is quite in accord with expectations. THF is a much better cation solvating agent than THP, so that one would expect more specific peripheral solvation of the barium cation

by THF, which would cause the two anions to open farther, as is the case.

It should be noted that the geometry assumed here for the salt is mathematically equivalent to one where the two anions are in parallel planes directly above each other, but twisted about  $\bar{R}$ , the line joining the two centers. In this model,  $\alpha$  would be the angle of twist of one ring relative to the other. That geometry, while formally equivalent, provides no rationale for the different values of  $\alpha$  in THF and THP, and so has been disregarded.

As a check on the accuracy of the theory, the distance  $R$  was determined by transforming the monomer spectrum (assuming sodium fluorenyl with a slight excess of crown ether to be a very good approximation of the unperturbed monomer in THP) as above, and the monomer transition moment evaluated by:

$$|\bar{M}|^2 = \frac{3\hbar e^2}{8\pi^2 mc} < \frac{f}{\tilde{\nu}} > = 2.126 \times 10^{-30} \frac{f}{< \tilde{\nu} >}$$

where  $f$  is the monomer oscillator strength, and  $< \tilde{\nu} >$  is the average wave number of the absorption band, determined by:

$$f = 4.319 \times 10^{-9} n \int \epsilon(\tilde{\nu}) d\tilde{\nu}$$

$$< \tilde{\nu} > = \int \tilde{\nu} \epsilon(\tilde{\nu}) d\tilde{\nu} / \int \epsilon(\tilde{\nu}) d\tilde{\nu}$$

where the term involving  $n$ , the refractive index ( $= 1.4200$  for THP), is a correction for medium effects.<sup>86</sup> Thus,  $\bar{M}^2$  was finally evaluated by:

$$|\bar{M}|^2 = 1.304 \times 10^{-38} \frac{(\int \epsilon(\tilde{\nu}) d\tilde{\nu})^2}{\int \tilde{\nu} \epsilon(\tilde{\nu}) d\tilde{\nu}} \text{ e.s.u.}$$

This value for the monomer,  $15.95 \times 10^{-36}$  e.s.u., was then used to

evaluate  $R^3$  according to the basic equation for the exciton splitting energy, which for the assumed geometry in THP is:

$$R^3 = \frac{2(1 + \cos^2 \alpha) |\bar{M}|^2}{\Delta E (1.9863 \times 10^{-16})}$$

where  $\Delta E$  is measured in  $\text{cm}^{-1}$ , and is equal to  $1940 \text{ cm}^{-1}$ ,  $1 + \cos^2 \alpha = 1.051$ , and the numerical factor converts  $\text{cm}^{-1}$  to ergs. This yields a value of  $R = 4.43 \text{ \AA}$  in THP, in fair agreement with expectations, considering the gross nature of the theory.

For the salt in THF,  $\Delta E = 1720 \text{ cm}^{-1}$ ,  $1 + \cos^2 \alpha = 1.235$ , which yields a value of  $R = 4.87 \text{ \AA}$ , quite in line with qualitative expectations.

A similar theoretical treatment is applicable to the hypochromism of these systems,<sup>87</sup> which predicts a dependence of the amount of hypochromism on the geometry of the aggregate. The theoretical treatment also requires knowledge about the oscillator strengths of other transitions, which are not known, so that it will not be considered further here.

Thus, the simple exciton interaction model gives good semi-quantitative results for this system. Attempts were made to apply the knowledge gained from the barium fluorenyl system to other systems thought to be aggregated: sodium fluorenyl in dioxane, and lithium fluorenyl in dioxane and toluene.

As would be expected for an aggregate, the fluorescence spectrum of all three of these salts is considerably quenched compared to a normal contact ion pair, good evidence in itself that all three are aggregated. However, unlike barium fluorenyl, the absorption spectra

show no exciton splitting so that it is difficult to make any quantitative statements about the structure of the aggregates. But one can use the fluorescence spectra to attempt to make some qualitative statements about the structure of the aggregates. See Figures 23-25.

For sodium fluorenyl in dioxane, the principal absorption maximum is at 354 nm, compared to 356 nm for the same salt in THP, a slight blue shift. Although an accidental cancelling of the geometrical factor cannot be ruled out, the most likely explanation is that the transition moment vectors are parallel and stacked. The fluorescence spectrum of sodium fluorenyl in dioxane (see Figure 36), beyond its low intensity, is quite similar to that of the same salt in THP, although very slightly red-shifted (maximum of 538 nm in THP, and 540 nm in dioxane), and contains little more helpful information. Indeed, the possibility that it is non-aggregated sodium fluorenyl that is emitting is not inconsistent with the experimental data, especially since the excitation and absorption spectra coincide.

For lithium fluorenyl in dioxane, the fluorescence spectra are more interesting. As noted above, the intensity is low relative to a "normal" contact pair, and the system has a shorter lifetime than would be expected. If one looks at the fluorescent maximum as a function of concentration one finds that it decreases as the concentration goes down, from 545 nm at  $1 \times 10^{-4}$  M to 540 nm at  $c < 10^{-6}$  M. Even more interesting are the excitation spectra, which have peaks at 345 nm and a shoulder at 360 nm, then at the lowest concentration show only a peak at 360 nm.

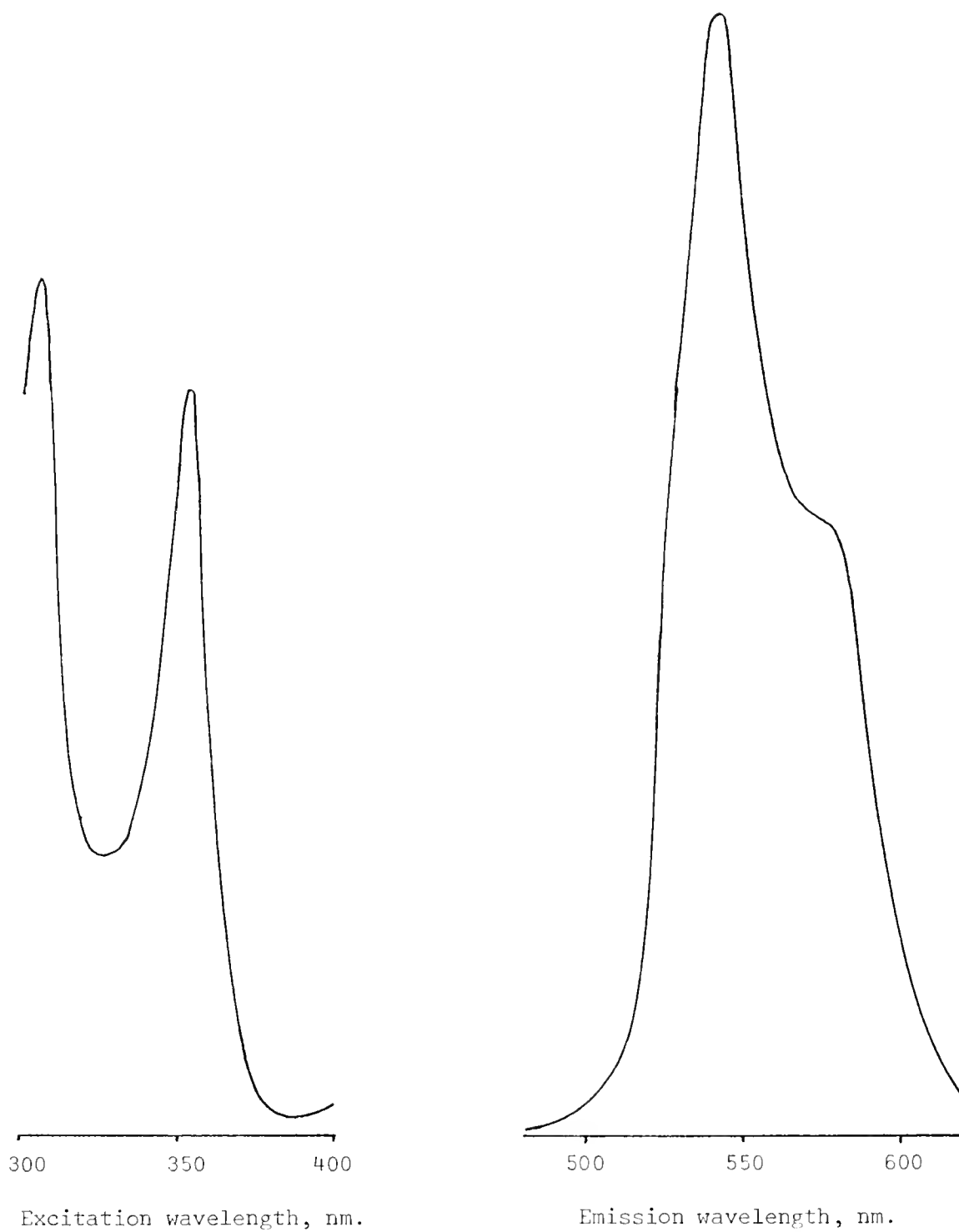


Figure 23. Excitation and emission spectrum of fluorenyl sodium in dioxane,  $[\text{NaFl}] = 8 \times 10^{-5} \text{ M}$ .

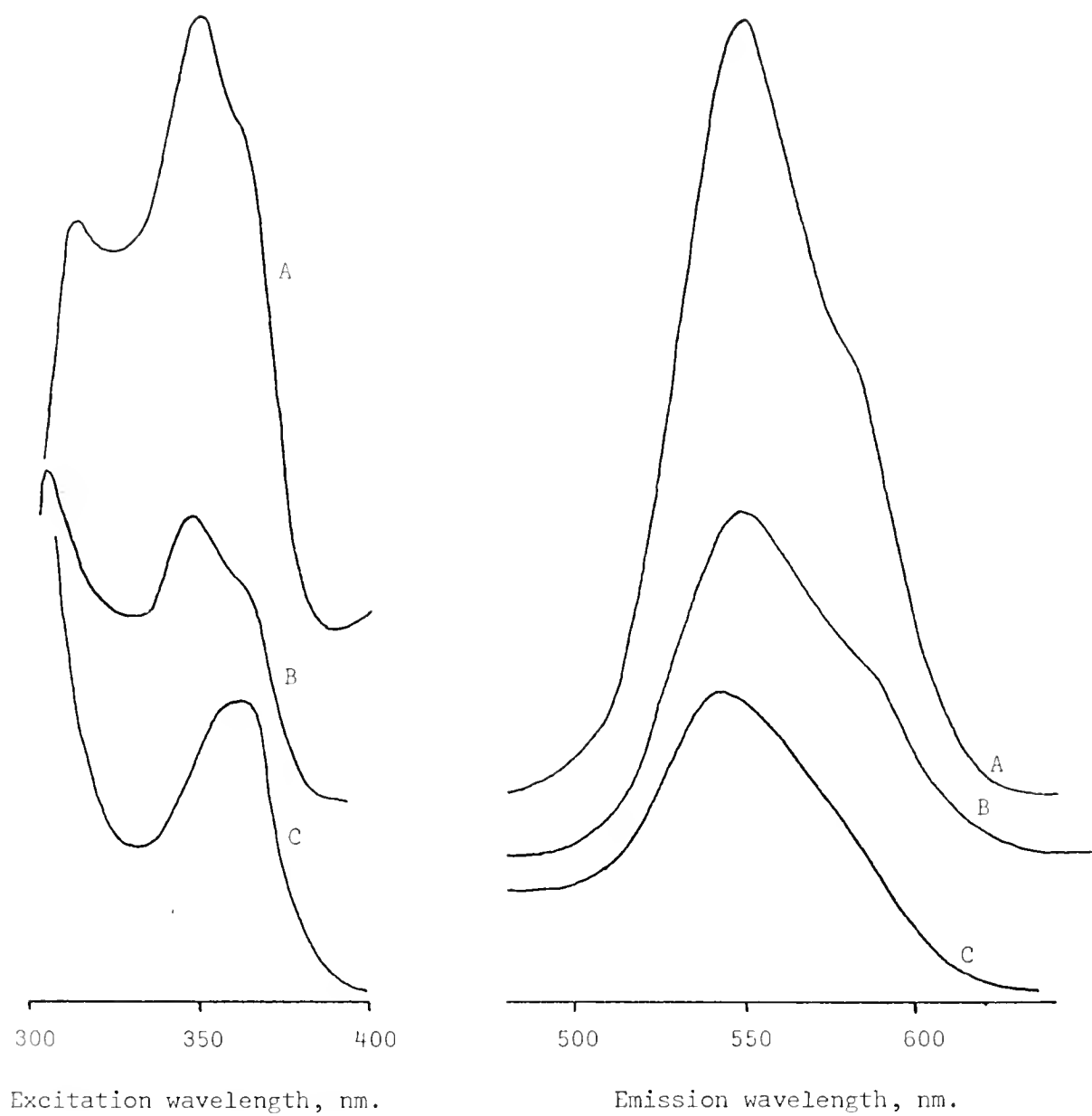


Figure 24. Excitation and emission of fluorenyl lithium in dioxane (not to scale). A.  $2 \times 10^{-4} \text{M}$ ; B.  $2.3 \times 10^{-5} \text{M}$ ; C.  $1 \times 10^{-6} \text{M}$ .

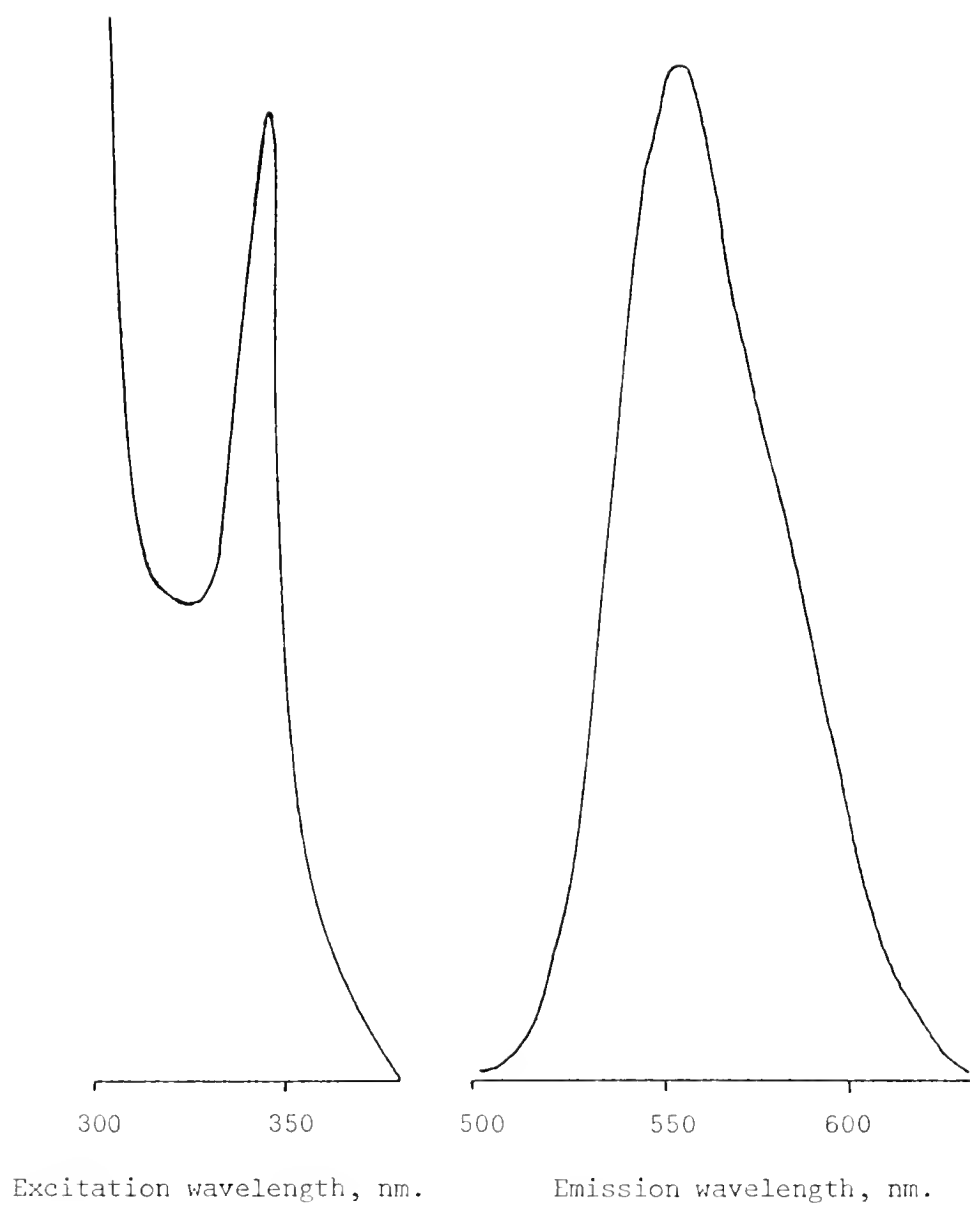
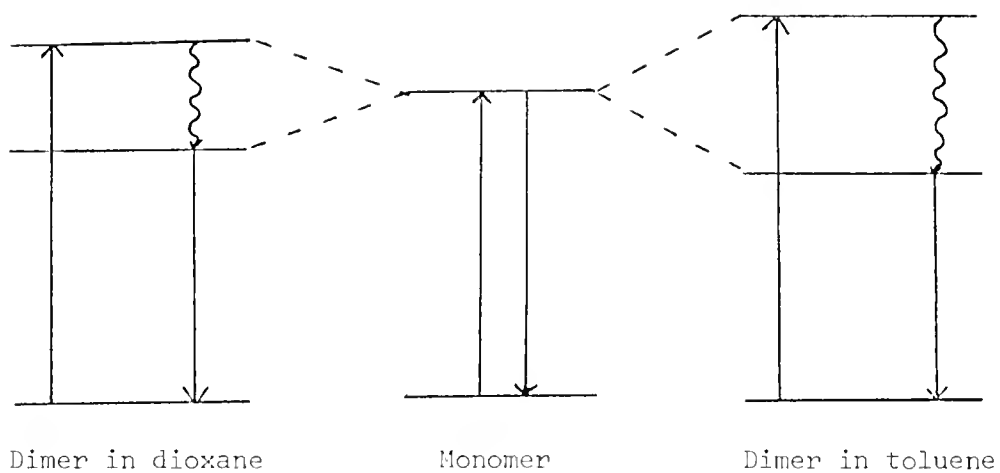


Figure 25. Excitation and emission spectrum of fluorenyl lithium, in toluene;  $[\text{LiFl}] = 1.1 \times 10^{-5} \text{M}$ .

There are two possibilities. Either one is seeing a change in the form of the oligomer to, presumably, a lower aggregation state, or one is seeing dissociation of the ion pair into free ions. To test for this, the spectra (both excitation and fluorescence) of fluorenyl cesium in dioxane were examined. This salt is known to be non-aggregated in dioxane,<sup>82</sup> so that it could provide a good test. If the anomalous peak appeared, it would be due to dissociation of the ion pair. If it did not appear, this would indicate that the effect was due to aggregation of the lithium salt in dioxane.

Over the concentration range  $5 \times 10^{-5}$  to  $1 \times 10^{-6}$  M, the emission and excitation spectra remained unchanged, indicating that the changes noted above, for fluorenyl lithium in dioxane, are probably due to changes in the state of aggregation, rather than dissociation into free ions.

Lithium fluorenyl in toluene should form even tighter aggregates than in dioxane, so that the above transition should be less likely to occur at a concentration that would allow it to be observed. As the fluorescence spectra show, this is the case. Throughout the concentration range, emission occurs at 552 nm, and the excitation maximum is at 344 nm. This is in qualitative agreement with the exciton splitting picture, since in dioxane, the distance between anions would be somewhat larger due to peripheral solvation thus decreasing the exciton splitting term relative to toluene. This would send the upper state higher and the lower state lower, causing absorption at a lower wavelength (343 nm vs. 346 nm) and emission at a higher wavelength (552 nm vs. 545 nm) in toluene relative to dioxane. This is depicted in Figure 26.



For absorption,  $\Delta E(\text{toluene}) > \Delta E(\text{dioxane})$ , thus:  
 $\lambda(\text{toluene}) = 343 \text{ nm} < \lambda(\text{dioxane}) = 346 \text{ nm}$ .

For emission,  $\Delta E(\text{toluene}) < \Delta E(\text{dioxane})$ , thus:  
 $\lambda(\text{toluene}) = 552 \text{ nm} > \lambda(\text{dioxane}) = 545 \text{ nm}$ .

Figure 26. The effect of solvent on the fluorenyl lithium aggregate.

For the fluoradenyl salts which are aggregated, the situation is much the same, although complicated by the greater number of bands, so that it is difficult to separate exciton splitting bands.

Barium fluoradenyl in THF has very clearly defined absorption bands due to a separated pair, as well as some ill-defined bands due to the anion in the aggregate. In THP, no contribution from the separated ion pair is apparent in the absorption spectrum.

The fluorescence spectrum of both these systems corresponds to the separated, or free, anion. While this is not too surprising for the salt in THF, it is not clear why this is true in THP as well. There is a considerable hypochromic effect on the absorption bands of the salt, larger than for the fluorenyl systems, so that fluorescence from the anion within the "aggregate" may be more effectively quenched than in the fluorenyl systems. The intensities of all the emission spectra were very low.

Lithium fluoradenyl in dioxane shows anomalies both in its absorption bands and in its emission spectra. There are ill-defined absorption bands at 354, 366, and 382 nm, compared to the other fluoradenyl salts (except barium) which have only two bands in this region. The probable explanation is exciton splitting of the normal band.

The fluorescence spectrum is very interesting since it is both excitation wavelength and concentration dependent. If excited at 355 nm at  $\approx 8 \times 10^{-5} M$  (a saturated solution), emission occurs at 591 nm; at  $1.3 \times 10^{-5} M$ , excitation at the same wavelength causes emission at 582 nm. Also, at  $8.1 \times 10^{-5} M$ , excitation at 382 nm causes emission at 582 nm, while at  $1.3 \times 10^{-5} M$ , this band, which is present in the absorption spectrum throughout, has disappeared from the excitation and emission pattern.

## CHAPTER VI GENERAL DISCUSSION AND SUMMARY

As has been seen, the concept of ion-pairing is just as valid in the excited state as in the ground state. In both states, there is an equilibrium between contact and separated pairs, which lies, for the excited state, farther toward the loose pair than in the ground state. This is a direct result of the different charge distribution in the excited state; for other systems, in which the charge becomes more localized at some atom, upon excitation the ion pairs might be tighter in the excited state.

### Cation and Solvent Effects

As in the ground state, it is possible to distinguish spectroscopically between contact and separated ion pairs, or between contact ion pairs and free ions, but it is not possible to distinguish separated ion pairs and free ions. Further, for the contact ion pairs the spectral shifts caused by different cations are smaller in the fluorescence spectra than in the absorption spectra. For example, fluorenyl sodium in THP absorbs at 355 nm compared to 373 nm for the separated ion pairs, a shift equivalent to  $1359\text{ cm}^{-1}$  (about 3.9 kcal/mole); the excited state system, (fluorenyl sodium)\* in THP, emits at 538 nm, compared to 528 nm for the separated pair, a shift of only  $352\text{ cm}^{-1}$  (about 1 kcal/mole).

The linear relationship between  $1/r_c$  ( $r_c$  the cationic radius) and  $\tilde{\nu}_{\text{max}}$ , the wave number at the maximum, observed by Horen Esch and Smid for fluorenyl absorption,<sup>39</sup> also holds for emission (see Figures 27 and 28). The plot for the fluorenyl system yields quite a reasonable value

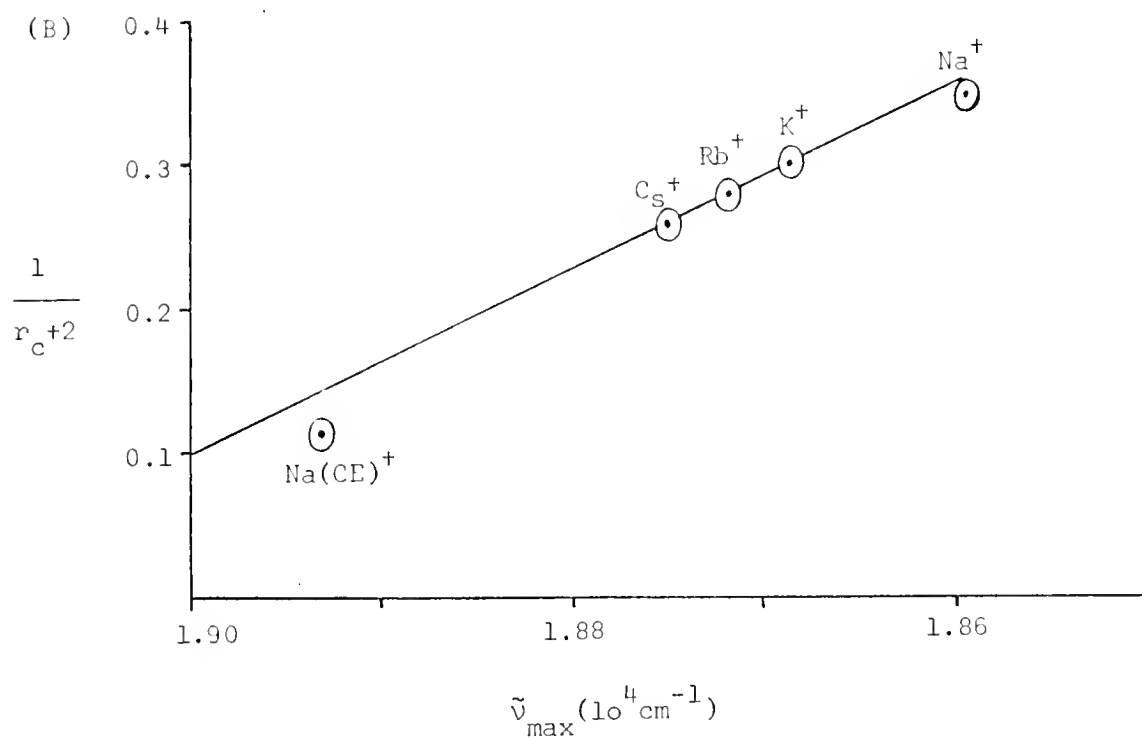
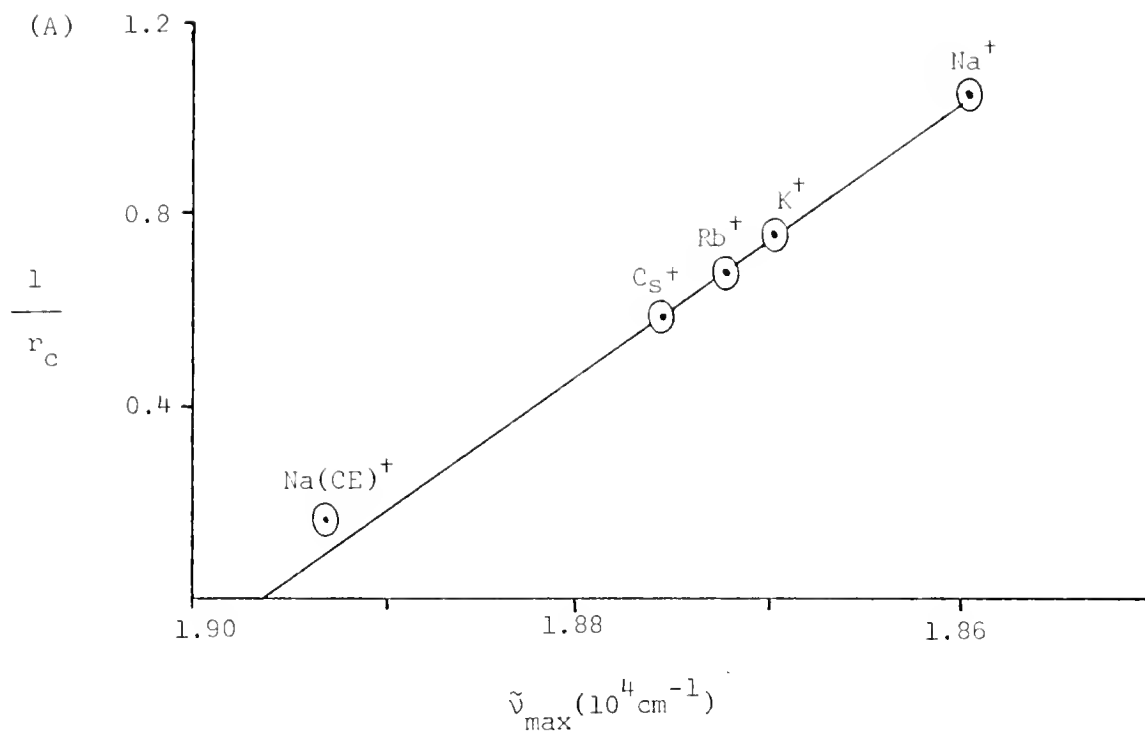


Figure 27. Plots of emission maximum vs. functions of the cationic radius, for the fluorenyl salts.  
 A.  $1/r_c$  vs.  $\tilde{\nu}$ ; B. Warhurst plot,  $1/r_c + 2$  vs.  $\tilde{\nu}$ .

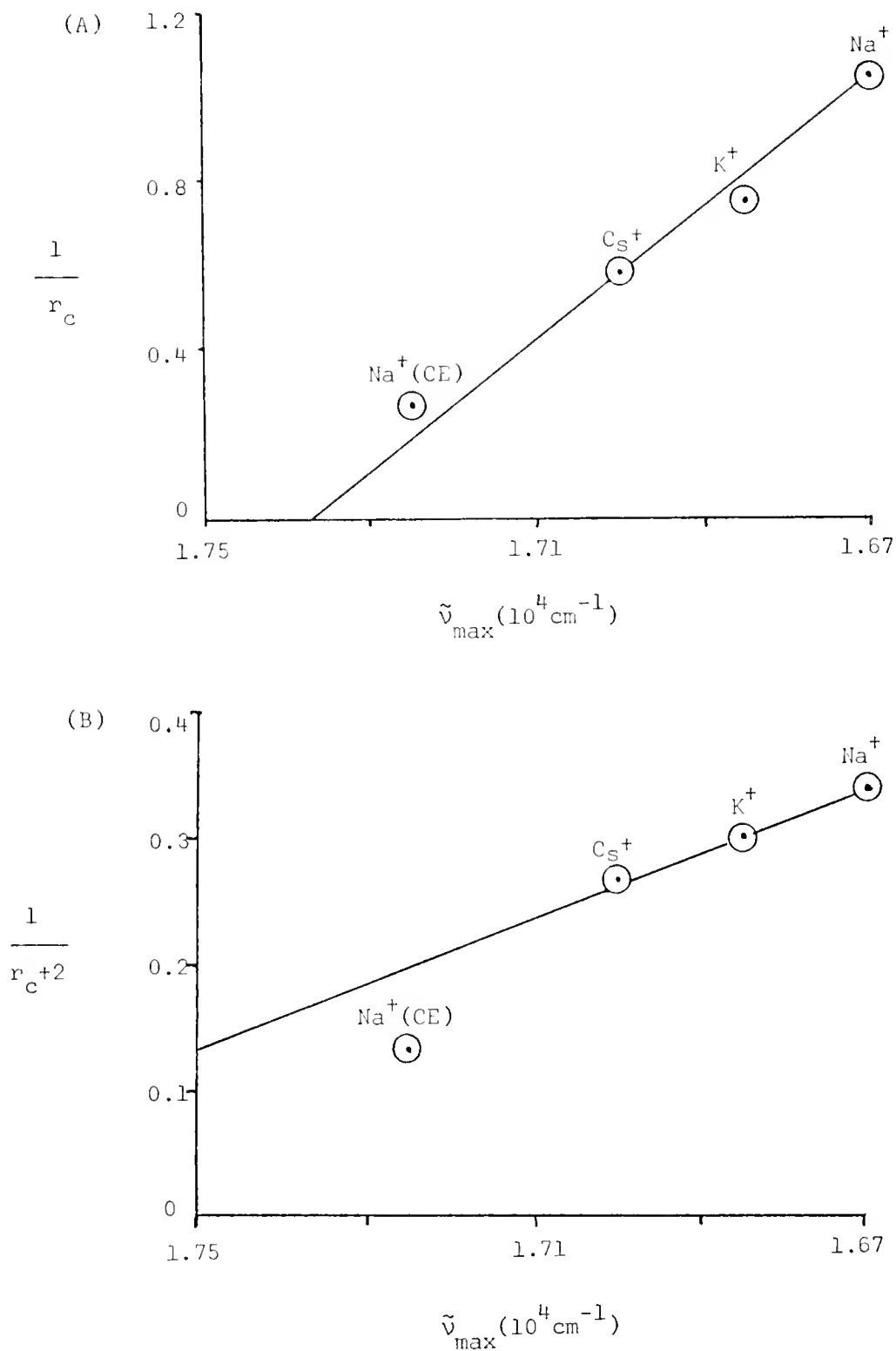


Figure 28. Plots of emission maximum as functions of cationic radius for the fluoradenyl salts. A.  $1/r_c$  vs  $\tilde{\nu}_{\max}$ . B.  $1/r_c+2$  vs  $\tilde{\nu}_{\max}$  (Warhurst plot).

for  $\lambda_{\text{max}}$  of the emission of the free ion, 527 nm; a Warhurst-type plot<sup>88</sup> of  $1/(r_c + 2)$  vs.  $\tilde{\nu}_{\text{max}}$ , while it gives a reasonable straight line, yields a much poorer value for  $\lambda_{\text{max}}$  of the free ion, 517 nm. For the fluorenyl systems, a value of 576 nm for the free ion's wavelength of maximum emission was extrapolated from the plot, while the Warhurst-type plot gave a value of 562 nm. (These plots were constructed assuming that the "cationic radius" of a separated ion pair was equal to the length of one molecule of THP and the radius of the sodium cation, 5.75Å.)

While there is little reason to expect one scheme to be better at predicting the spectral maximum than the other, it should be noted that the Warhurst model is much worse at describing the behavior of these systems.

The nature of the counterion affects not only the position of the emission maximum, but also the intensity and lifetime of that emission. From the data presented, one must conclude that the cation quenches the fluorescence of the excited anion in at least two ways. First, it can quench through a "normal" heavy atom effect, which is the predominant effect in cesium salts, presumably by increasing spin-orbit coupling from the excited singlet to the triplet state. This effect should decrease as the atomic number of the cation decreases.

The cation may also quench the excited anion through a mechanism involving some perturbation of the rigid, planar anion, which depends on the size of the cationic field for its effectiveness, increasing as the cationic radius decreases. Although no firm conclusion about the nature of this other effect can be reached on the basis of the present work, some of the factors involved can be mentioned. (For convenience, the anion discussed will be the fluorenyl anion.)

In general, the rate constant for non-radiative deactivation of the excited state is proportional to:<sup>89</sup>

$$(\sum_k \langle \phi_1 | \frac{\partial}{\partial Q_k} | \phi_o \rangle F_k)^2$$

where  $\phi_o$ ,  $\phi_1$  are the ground and excited state wave functions, respectively,  $Q_k$  is the k'th normal vibration mode of the molecule, and  $F_k$  is a vibrational term involving the Franck-Condon coupling factor.

One would expect the energy of the cation-anion vibration to increase as the radius of the cation decreased, thus requiring fewer vibrational quanta to deactivate the excited state. Thus, the effect of the cation on the purely vibrational part of the above expression,  $F_k$ , would be similar in nature to the effects seen in substituting deuterium for hydrogen in aromatic hydrocarbons<sup>90,91</sup> (Deuterated forms have longer lifetimes and higher quantum yields.), with this effect greater for sodium than potassium, etc.

Perhaps more significant would be the effect of the cation on the electronic factor,  $\langle \phi_1 | \partial / \partial Q_k | \phi_o \rangle$ . As indicated in Appendix 2, charge density is more dispersed into the benzene rings for the excited state free anion, while it is concentrated in the cyclopentadienyl ring in the ground state of the free anion. The cation may reasonably be expected to polarize the  $\pi$ -electron system and draw charge density toward itself. No matter what position the cation occupies relative to the excited anion, this effect should alter the excited state wave function, and hence the amount of coupling between it and the ground state wave function via any of the vibrational modes. Particularly affected should be skeletal vibrational modes of the conjugated system. Since there apparently is such a vibration coupled to the electronic

transition (the vibration responsible for the second peak in the fluorescence spectra), and (from Figure 7) there is some variation of relative peak heights with cation, this could be an important factor in deactivating the excited state, which increase in importance as the cationic radius decreases, i.e. sodium should polarize the anion more than cesium.

Another possible mechanism is one involving electron transfer from the anion to the metal cation (similar to that observed for the quenching of anthracene fluorescence by inorganic anions<sup>70</sup>). This would be expected to increase in importance as the cationic radius decreased, or as the electron affinity of the cation (=ionization potential of the metal) increased. Recent work on the quenching of carbazole (a system isoelectronic to the fluorenyl anion)<sup>37,93</sup> indicates that quenching by proton donors is less important than quenching by electron acceptors for carbazole. For the fluorenyl or fluoradenyl salts, the formation of an ion pair would be a necessary prerequisite for such a mechanism to hold true. Recently, such a mechanism was invoked to explain non-Stern-Volmes behavior in the quenching of the short-lived phosphorescence of ruthenium (II) complexes by anionic coordination complexes.<sup>92</sup> Assuming that the additional quenching was kinetically controlled by the ion pair association-dissociation equilibrium, the authors were able to derive reasonable dissociation constants.

As is readily apparent, little has been done to quantify the effects of ion-pairing on lifetime, quantum yield, or other properties of the excited state. Such a study, coupled with data on the phosphorescence of these compounds, could go far to help explain the storage and transfer of electronic energy in solution, especially since the effect of chemical parameters on the ion-pairing has been so extensively studied.

Intimately connected to the quenching mechanisms is their virtual elimination upon the addition of crown ether. This effect is especially dramatic for the bisfluorenyl barium salt. In THF, in the absence of crown ether, emission is due to the free anion and the contact-"aggregate," with no evidence for emission from the free  $\text{Ba}^{2+}\text{Fl}^-$  species. Upon addition of crown ether, emission occurs not only from the separated pair, but also from the species  $(\text{CE})\text{Ba}^{2+}\text{Fl}^-$ . One is forced to ask why the emission intensity of these two species is so different.

Suppose the barium ion rapidly resonates through the crown ether cavity,<sup>41</sup> between the two anions. The presence of the crown ether will decrease the energy of the barium cation-fluorenyl anion vibration (i.e. the "bond" between the two will not be as tight), decrease its ability to act as an electron acceptor, decrease its ability to polarize the anion, and decrease the overlap between the lowest vacant orbitals on the barium cation and the highest occupied orbitals of the fluorenyl anion (since the crown ether will be putting charge density onto the cation). Thus, no matter what the mechanism of cation quenching, the barium-crown ether complex should be much less effective as a quencher than the uncomplexed barium ion. The free  $\text{Ba}^{2+}\text{Fl}^-$  ion probably has the barium cation embedded in the anion, thus increasing its effectiveness as a quencher.

To this point, no effect of solvent has been considered. It has been seen in previous chapters that the same solvent effects observed in the ground state of these salts are observed in the excited state. In order to more firmly establish the explanation given as the proper one for these systems, attempts were made to correlate the spectral behavior of these salts with some of the most widely used schemes in the literature for non-specific solvent effects.

As shown by Hogen Esch and Smid,<sup>13,39</sup> there is no correlation with Kosower's Z-value of solvent polarity,<sup>94</sup> or dielectric constant. Another scheme, due to Lippert,<sup>95</sup> attempts to correlate the Stokes shift (difference between the 0,0 absorption and fluorescence bands) in wave numbers of the chromophore with:

$$\frac{2(\mu_e - \mu_g)^2}{hca^3} \left[ \frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \right]$$

where  $\mu_e$ ,  $\mu_g$  are the dipole moments of the excited and ground state species,  $\epsilon$  is the static dielectric constant,  $n$  the index of refraction of the solvent, and  $a$  is the Onsager radius. Assuming the Stokes shift can be approximated by the difference between the longest wavelength absorption and shortest wavelength fluorescence maxima, a plot of  $\Delta\tilde{\nu}$  vs. the quantity in brackets should be linear with a slope proportional to  $(\mu_e - \mu_g)^2$ . As Figure 29 shows, there is no such linearity.

Thus the experimental results obtained can not be explained on the basis of any non-specific solvent effect, but rather can only be explained in terms of the specific interactions of ionic species with solvent molecules. For cations, this manifests itself in the increasing proportion of separated ion pairs as the solvent is changed from one that solvates cations poorly to one with greater cation solvating ability, or as the cationic radius is decreased. For anions, while there is apparently little interaction with aprotic solvents, with protic solvents hydrogen bonding to the anion is seen. In systems such as mixtures of n-propanol and THP, one sees solvent-shared species, since complexation of the cation with crown ether disrupts the hydrogen bonding.

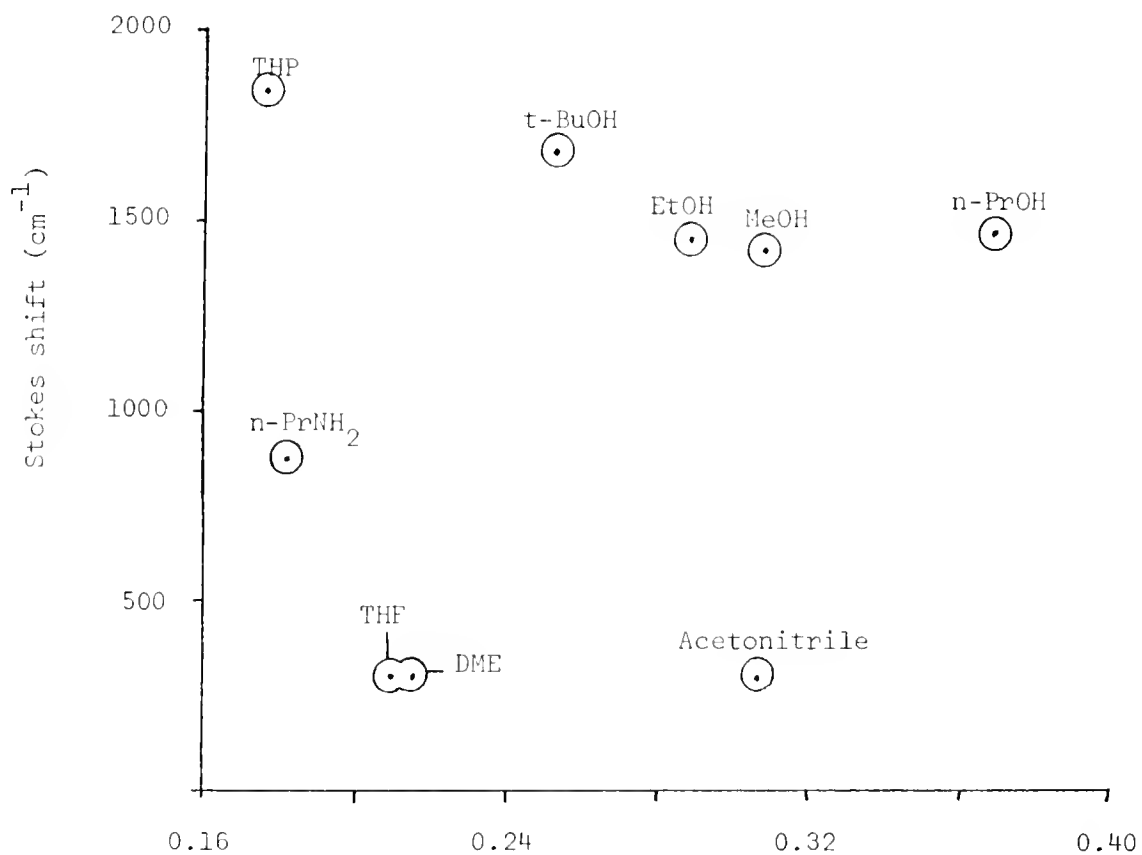


Figure 29. Plot of Stokes shift of fluoradenyl sodium as a function of Lippert's measure of solvent polarity.

### Radical Anions

In view of the apparent generality of the concept of ion-pairing for both the ground and excited state in low dielectric constant media, it is surprising that such effects have not been taken into account when considering excited state processes. Weller, et al., in a series of papers on charge transfer complexes in the excited state,<sup>31-36</sup> examined the equilibria which occurred upon mixing of radical anions with radical cations. Implicit in their work is the assumption that their radical salts are free ions<sup>96</sup> and yet they work in such solvents as DME, THF and 2-methyl-tetrahydrofuran (MTHF), with the sodium salt of the radical anion and radical cation-perchlorate salts. While the state of ion pairing of the radical cation-perchlorate may not be well known, the state of ion pairing for sodium-radical anion salts has been extensively studied by Szwarc, and others,<sup>18</sup> for anions which Weller investigated, such as the anthracene anion.

Weller concluded that his data were most consistent with the following scheme:

$$\begin{array}{c}
 {}^2\text{A}^{\cdot-} + {}^2\text{D}^{\cdot+} \xrightleftharpoons{K_D} ({}^2\text{A}^{\cdot-} || {}^2\text{D}^{\cdot+}) \xrightleftharpoons{K_1} {}^1(\text{A}^{\cdot-}\text{D}^{\cdot+})^{\ddagger}, \text{ where increas-} \\
 \text{non-fluorescent} \\
 \quad \quad \quad \updownarrow^{K_2} \\
 {}^1\text{A}^{\cdot\ddagger} + \text{D}
 \end{array}$$

ing solvent polarity would cause decreases in the chemiluminescent intensity and lifetime of  ${}^1(\text{A}^{\cdot-}\text{D}^{\cdot+})^{\ddagger}$  by shifting equilibria 1 and 2 toward the (presumed) non-fluorescent  $({}^2\text{A}^{\cdot-} || {}^2\text{D}^{\cdot+})$  solvent-shared ion pair, while decreases in temperature would have the opposite effect.

The work reported here on the alkali metal salts of anthracene calls into question the independent existence of such a species as  $({}^2\text{A}^{\cdot-} || {}^2\text{D}^{\cdot+})$ . As has already been discussed, the proportion of separated

ion pairs increases as the cation is changed from a larger to a smaller one, so that if cesium, with its much smaller size and consequent greater cationic field, is not separated, it is highly unlikely that the much larger aromatic radical cations employed by Weller would form separated ion pairs.

An alternative approach would take into account the effect of the metal cation on the reactivity of the radical anion. In solvents such as those used by Weller, the metal cation-radical anion salts will be primarily contact ion pairs,<sup>18</sup> and the reaction taking place will be a displacement of the metal cation by the radical cation. As the temperature is decreased, the proportion of separated pairs ( $M^+ || A^{\cdot -}$ ) increases,<sup>18,39</sup> thus making the metal ion less competitive, and increasing the amount of  $^1(D^+A^-)^*$ , so that one would expect to see large increases in the relative intensity of the fluorescence of  $^1(D^+A^-)^*$ . This, indeed, Weller sees.<sup>35</sup> It must be stressed that this is in direct contradiction to what would be expected on the basis of solvent polarity (if one accepts Weller's scheme) since decreasing temperature increases solvent polarity.<sup>18</sup> In further apparent contradiction to his views on the effect of solvent polarity, Weller finds increased chemiluminescent intensity in DME relative to MTHF, although DME is the more polar solvent. The proposed alternative explains this by pointing out that in DME, there will be a larger proportion of separated ion pairs ( $M^+ || A^{\cdot -}$ ) than in MTHF, hence more  $^1(D^+A^-)^*$ .

It was not the aim of the present study to establish this alternative mechanism. However, the present work would seem to indicate that such radical systems deserve much greater attention than they have heretofore received, especially in view of the great deal of attention

being given electrochemiluminescent reactions, which are usually run in the presence of supporting electrolyte. In view of the above discussion, it may be quite important to study the effect of the supporting electrolyte carefully, taking ion pairing into account, in order to achieve optimum luminescence yields.

### Aggregation Effects

As theory would predict,<sup>6-8</sup> the intensity of the fluorescence from the aggregated systems studied is considerably lower than that of non-aggregated systems. In general, the aggregate has been found to fluoresce to the red (lower energies) of its monomeric form, as expected if the weak coupling of exciton theory is considered.<sup>6-8</sup> More interestingly, the excitation spectra of some of the aggregated systems, bisfluorenyl barium in THP and fluorenyl lithium in dioxane, display new peaks not found in the absorption spectra of these systems. It would seem that either there is a new species, perhaps corresponding to a different state of aggregation with a higher quantum yield, or the quantum yield of the aggregate is not constant for all wavelengths. In any event, the present work shows that, by helping identify the species present, the fluorescence spectra of these ion pairs can aid exciton theory in determining the structure and nature of these aggregates (This is apparently the first time that exciton theory has been applied to carbanionic systems.).

Indeed, the methods used above may clear up certain anomalies previously observed. Exner, et al.,<sup>10</sup> in studying the effect of solvent on the ion pair interaction of 9-(2-hexyl) fluorenyl lithium found that the contact pair absorbed at 358 nm (in diethyl ether) and the solvent-separated ion pair absorbed at 387 nm (in THF). However, in hydrocarbon

solvents (hexane, cyclohexane, benzene) the absorption maximum was at 368 nm. This is easily understood if one assumes the aggregate to be composed of rings in parallel planes, as for fluorenyl lithium in toluene. Unlike the fluorenyl salts, however, the alkyl substituents at the 9-position would force the molecule into an antiparallel arrangement of the transition dipoles, resulting in the low energy component being completely allowed, while the high energy component is completely forbidden, i.e. a red shift of the absorption band relative to the monomer.

It has also been shown that addition of a complexing agent (crown ether) to an anion-dimer (bisfluorenyl barium) results in large increases in the fluorescent intensity. The effect of counterion on the structure of ionic dye aggregates has received almost no attention. In fact, for the fluorescein-derived anionic dyes, it has been maintained that there is no effect of counterion<sup>2</sup> (though on shaky ground), and any possible part it might play in holding the aggregate together ignored. Addition of crown ethers to the fluorescein anion aggregates could be of importance in improving the performance of dyes in such areas as lasers and photographic film, both by vitiating cation quenching effects and by decreasing the amount of interaction between anion units.

### Ionization

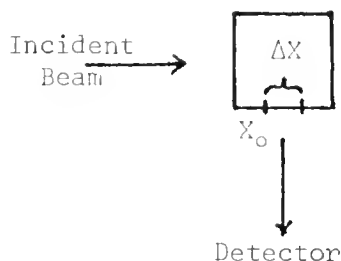
As previously noted, no excited free ions were observed unless they were present in the ground state. In general, though thermodynamically allowed (as indicated by Förster cycle calculations), excited state dissociation of ion pairs, or of covalently bonded hydrocarbon acids, is not allowed because of kinetic factors.

An interesting example of this is the difference between excited states produced chemically and photochemically, as investigated by White, et al.<sup>30</sup> Under most circumstances, the chemiluminescence caused by the oxidation of luminol to the excited 3-aminophthalate dianion is identical to the fluorescence of the dianion. However, in aqueous dimethyl sulfoxide (DMSO), the two spectra differ, since the ground state environments of the species emitting will be different: as would be expected, the chemiluminescence spectrum reflects a lower amount of ion-pairing produced from the transition state of the reaction compared to the fluorescence of the directly excited 3-aminophthalate ion.

Because of this reflection of the ground state environment, excited state work can be quite useful in investigating ionic equilibria in solution. As has been seen, since no excited state ionization of ion pairs is consistent with the data, the ionization observed must occur in the ground state. For most of the systems studied, ground state ionization is not easily observed spectroscopically; the fluorescence spectra, and especially the excitation spectra, allow access to a much greater concentration range than here-to-fore possible.

# APPENDIX 1 INNER FILTER EFFECTS

Assume an experimental design as shown below, with an incident beam of intensity  $I(0, \lambda_i)$ , at a wavelength of  $\lambda_i$ , passing into a square cell, one centimeter on a side. Assume the monochromator for the emitted light "sees" a region starting from point  $X_0$ , extending to  $X_0 + \Delta X$ , and that the fluorescent beam is not reabsorbed.



Let  $I(X, \lambda_i)$  be the intensity of the exciting beam at a distance  $X$  from the front wall of the cell. If the concentration of the sample solution is  $c$ , and the molar extinction coefficient for the absorption at  $\lambda_i$  is  $\epsilon_i$ , then:

$$I(X_0, \lambda_i) = I(0, \lambda_i) \exp(-\epsilon_i X_0 C) \text{ and}$$

$$I(X_0 + \Delta X) = I(0, \lambda_i) \exp(-\epsilon_i X_0 C) \exp(-\epsilon_i \Delta X C)$$

The amount of light absorbed in this region will be  $I(X_0, \lambda_i) - I(X_0 + \Delta X, \lambda_i)$ , or,  $I(0, \lambda_i) \exp(-\epsilon_i X_0 C) [1 - \exp(-\epsilon_i \Delta X C)]$ .

The measured fluorescent intensity,  $F_i$ , is given by:

$$F_i = k \phi_i (\text{amount of light absorbed})$$

where  $k$  is a constant to account for instrumental effects, and  $\phi_i$  is the quantum yield. If one compares the fluorescent intensity produced by two different wavelengths, one at an absorption maximum, the other at an absorption trough, for high and low concentrations, one finds interesting contrast.

Suppose  $X_0 = 0.5$ ,  $\Delta X = 0.1$ , merely for convenience, and look at the emission of fluorenyl sodium in THP. If  $\lambda_1 = 356$  nm,  $\epsilon_1 = 12000$ ;  $\lambda_2 = 392$  nm,  $\epsilon_2 = 120$ . Assuming the quantum yield to be a constant, for all  $\lambda_i$ ,

$$\frac{F_1}{F_2} = \frac{\exp(\epsilon_2 C/2)}{\exp(\epsilon_1 C/2)} \cdot \frac{1 - \exp(-\epsilon_1 C/10)}{1 - \exp(-\epsilon_2 C/10)}.$$

$$\text{At } C = 1 \times 10^{-6} \text{M}, \quad \frac{F_1}{F_2} = \frac{\exp(6 \cdot 10^{-5})}{\exp(6 \cdot 10^{-3})} \cdot \frac{1 - \exp(-1.2 \cdot 10^{-3})}{1 - \exp(-1.2 \cdot 10^{-5})} \approx 100,$$

as is seen in both the absorption and excitation spectra. At  $C = 1 \cdot 10^{-3} \text{M}$ , on the other hand,

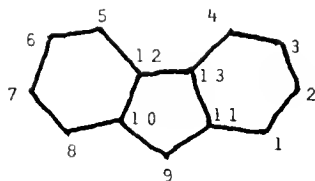
$$\frac{F_1}{F_2} = \frac{\exp(0.06)}{\exp(6)} \cdot \frac{1 - \exp(-1.2)}{1 - \exp(-0.012)} \approx 0.15.$$

Thus, at this concentration, 392 nm is a much better excitation wavelength than the absorption maximum. As the concentration is increased still further, the ratio  $F_1/F_2$  should approach 0. At  $2 \times 10^{-2} \text{M}$ , the excitation spectrum of the salt indicates that virtually no observable emission is caused by excitation at 356 nm. These changes may be qualitatively seen in Figure 8, which shows the effect of concentration on the excitation spectrum of fluorenyl sodium in THP. The relations

above can, semiquantitatively, describe the effect of concentration on the excitation spectrum.

APPENDIX 2  
POPULATION ANALYSIS OF THE FLUORENYL  
ANION BASED ON HÜCKEL CALCULATION

The numbering of the fluorenyl anion is as follows:



Assuming  $C_{2v}$  symmetry for the anion, Table A1 shows the relative orbital energies (if there is no overlap;  $S=0$ ). Table A2 compares the  $\pi$ -electron population in the ground and first excited state. Note that in the first excited state, the cyclopentadienyl system (atoms 9-13) has less than half the  $\pi$ -electron density of the ground state. (Preliminary INDO calculations uphold the validity of the model presented here.)

TABLE A1: ENERGY LEVELS AND ORBITAL SYMMETRIES  
(IN UNITS OF  $\beta$ )

<u>ORBITAL</u>	<u>E(S=0)</u>	
$b_1$	2.4687	
$a_2$	1.8912	
$b_1$	1.4142	
$b_1$	1.2931	
$a_2$	1.0000	
$a_2$	0.7046	
$b_1$	0.1811	occupied
<hr/>		
$b_1$	-0.8118	empty
$a_2$	-1.0000	
$a_2$	-1.3174	
$b_1$	-1.4142	
$b_1$	-2.1311	
$a_2$	-2.2784	

---

TABLE A2: POPULATION ANALYSIS OF THE FLUORENYL ANION

<u>ATOM NO.</u>	<u>NO. OF <math>\pi</math> ELECTRONS</u>	
	<u>(Fl<sup>-</sup>)</u>	<u>(Fl<sup>-</sup>)<sup>‡</sup></u>
1,8	1.0579	1.0793
2,7	1.0294	1.1379
3,6	1.0764	0.9887
4,5	1.0088	1.1485
9	1.3221	0.9749
10,11	1.0562	1.0571
12,13	1.1103	1.1027

APPENDIX 3  
EVIDENCE FOR THE AGGREGATION  
OF FLUORADENE IN PROTIC SOLVENTS

Let R be the hydrocarbon monomer, R\* the excited monomer, D\* the excimer, and  $I_X$  the intensity of the emission from X. If, as in the experiments reported in the text, there is a continuous flow of radiation, the following processes may take place.

- (1) Excitation:  $R + h\nu \xrightarrow{k_x} R^*$
- (2) Radiationless decay:  $R^* \xrightarrow{k_{rR}} R$
- (3) Monomer fluorescence:  $R^* \xrightarrow{k_{fR}} R + h\nu'$
- (4) Excimer formation:  $R^* + R \xrightarrow{k_D} D^*$
- (5) Excimer fluorescence:  $D^* \xrightarrow{k_{fD}} D + h\nu''$
- (6) Radiationless decay of the excimer:  $D^* \xrightarrow{k_{rD}} R + R$

Assume a steady state for D\*, i.e.

$$(7) \frac{d[D^*]}{dt} = 0$$

$$I_R = k_{fR}[R^*]$$

$$I_D = k_{fD}[D^*]$$

Let  $R_e$  be defined so that at  $[R] = R_e$ ,  $I_R = I_D$ . From (7),

$$(8) \frac{d[D^*]}{dt} = 0 = k_D[R^*][R] - k_{fD}[D^*] - k_{rD}[D^*]$$

Solving (8) for  $[D^*]$  gives:

$$[D^*] = \frac{k_D[R][R^*]}{k_{fD} + k_{rD}}$$

At  $[R] = Re$ ,  $k_{fR}[R^*] = k_{fD}[D^*] = \frac{k_{fD}k_D[R][R^*]}{k_{fD} + k_{rD}}$ . Thus,  $k_{fR} = \frac{k_{fD}k_D}{k_{fD} + k_{rD}}$

Re, or, rearranging,  $Re = \frac{k_{fR}}{k_D} [1 + (k_{rD}/k_{fD})]$ . In hexane,  $Re \sim 1 \times 10^{-3} M$ ;

in ethanol, only the excimer is seen, so that  $Re < 10^{-7} M$ . The ratio

$\frac{k_{rD}}{k_{fD}}$  should be relatively independent of the nature of the solvent, so

$$\text{that } \frac{Re(\text{ethanol})}{Re(\text{hexane})} \approx \frac{k_{fR}/k_D(\text{ethanol})}{k_{fR}/k_D(\text{hexane})} < \frac{10^{-7}}{10^{-3}} = 10^{-4}.$$

While the possibility of hydrogen bonding by ethanol to the hydrocarbon excimer cannot be ignored (increasing  $k_{rD}$  in ethanol compared to hexane), this would tend to increase  $Re(\text{ethanol})/Re(\text{hexane})$  and so need not be considered. A more important consideration is the effect of changing solvent on  $k_D$ . If the solute is evenly dispersed throughout the sample, for initially monomeric species, the rate constant for excimer formation is usually assumed to be diffusion controlled,<sup>62,97</sup> which seems a reasonable assumption in hexane. But if this is true for ethanol, it follows that a diffusion-controlled process in ethanol will occur  $10^4$  times faster than in hexane. This is eminently silly, especially since hexane is less viscous than ethanol at room temperature.<sup>71</sup>

An obvious explanation is that, in ethanol, the hydrocarbon is not dispersed evenly throughout the sample, but is aggregated. This would also help explain the behavior of fluoradene in alkoxide/alcohol solutions reported by Streitweiser, et al. (and replicated in the present study).<sup>77</sup> These workers saw formation of macroscopic particles as the base concentration approached 1M. This points to an unfavorable interaction between solute and solvent, which would be eased by aggregate formation.

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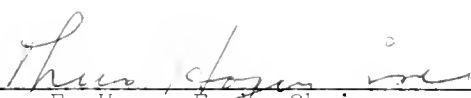
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## BIOGRAPHICAL SKETCH

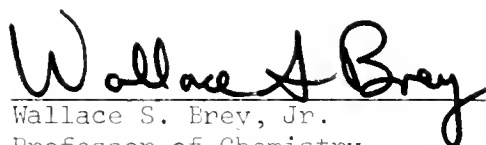
M. John Plodinec was born March 29, 1946, in Kansas City, Missouri. After living in Kansas and Connecticut, he moved to Villanova, Pennsylvania, with his family, and graduated from Harrison High School, in Rosemont, Pennsylvania, in 1964. He attended Michigan State University for two years, then transferred to Franklin and Marshall College, Lancaster, Pennsylvania, where he graduated in 1968, with a Bachelor of Arts in Chemistry. After one year of graduate study at the University of Florida, his career was interrupted by two years of keeping America safe from democracy.

He is married to the former Louise Robinson, and has a son and a daughter.

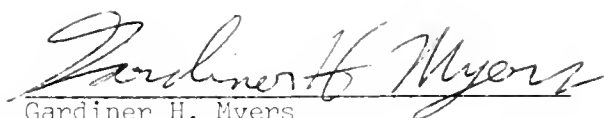
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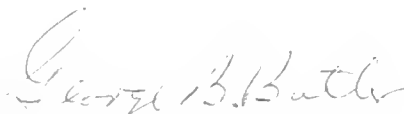
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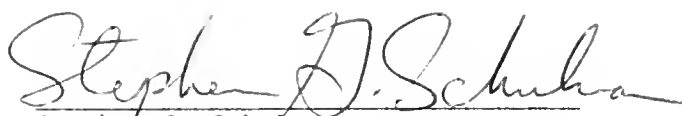
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Assistant Professor of Pharmaceuti-  
cal Chemistry

This dissertation was submitted to the Graduate Faculty of the Department of Chemistry in the College of Arts and Sciences and to the Graduate Council, and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

December, 1974

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